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CIVIL ENGINEERING CORROSION CONTROL
VOLUME I. CORROSION CONTROL - GENERAL

HINCHMAN CORPORATION

PREPARED FOR
AIR FORCE CIVIL ENGINEERING CENTER

JANUARY 1975

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Block 20 - Abstract (Cont'd)

corrosion problems encountered on real property and real property installed equipment.

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AFCEC-TR-74-6, Volume 1

CIVIL ENGINEERING CORROSION CONTROL
VOLUME I - CORROSION CONTROL - GENERAL

by

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FOREWORD


This report summarizes work done between May 1972 and Nov 1974. Thomas F. Lewicki was Project Officer. The major portion of the information in this report was compiled by the Hinchman Company under Investigation Engineering Project IE 16-72-1, contract number F53615-72-C-0400, from sources listed in the acknowledgements section of this report. The authors contributed the remainder of the information for this report.

This report is published in three volumes, Volume I - Corrosion Control - General, Volume II - Cathodic Protection Testing Methods and Instruments, and Volume III - Cathodic Protection Design.

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This technical report has been reviewed and is approved for publication.


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PREFACE

The Air Force's major guide to corrosion control of real property and real property installed equipment has been contained in Air Force Manual 88-9, Chapter 4 which was published August 1962. The corrosion control field has been progressing with new methods, materials and equipment constantly being introduced. Since the Air Force's corrosion manual was old and outdated, a need existed for searching, investigating and documenting the new methods, materials and equipment for corrosion control. It was decided that the most prompt and economical method of accomplishing this task was by procuring the services of a prominent corrosion engineering firm. Because of the large volume of the documented findings of this endeavor, the information has been published in three volumes. The first volume is entitled Corrosion Control - General. The second and third volumes are entitled Cathodic Protection Testing Methods and Instruments and Cathodic Protection Design.

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Sections of this report have been prepared from material found in AFM 88-9, Chapter 4 "Corrosion Control" (1 August 1962) and Designing Impressed Current Cathodic Protection Systems with Durco Anodes, edited by William T. Bryan, The Duriron Company Inc., Dayton, Ohio, 1970. In addition, the following sources have provided data found in tables and figures, sometimes revised or updated:

<u>Figure</u>	<u>Source</u>
3-3, 3-4, 3-5, 4-6, 4-8, 4-9, 4-11, 4-14, 4-22, 4-23, 4-26, 5-6	AFM 88-9, Ch. 4 (1 August 1962)
4-20	The International Nickel Co., Inc. Francis L. LaQue Corrosion Laboratory
5-1	Owens-Corning Fiberglas Corp.
5-24	Department of the Army, Corps of Engineers

<u>Table</u>	<u>Source</u>
3-1, 3-2, 3-3, 5-1, 5-2, 5-3, 5-4, 5-5, 5-6, 5-7, 5-8, 5-9	AFM 88-9, Ch. 4 (1 August 1962)
5-10, 5-11	Johns - Manville Corp.
5-12	Cathodic Protection, Lindsay M. Applegate, Copyright 1960 Mc-Graw-Hill, New York
5-13	Marshall Parker, The Works of

CORROSION CONTROL - GENERAL

SECTION 1 - INTRODUCTION

1.1 PURPOSE. This report is specifically written for Civil Engineering personnel but will be used by all elements of the Military. It covers mainly Real Property and Real Property Installed Equipment.

1.2 SCOPE. This is a report on corrosion and corrosion control of buried and submerged metal structures. Causes and theory of corrosion, as well as cathodic protection application, material selection, and some coatings are included.

1.3 IMPLEMENTATION. The report is a guide, based on the best information currently available.

SECTION 2 - JUSTIFICATION FOR CORROSION CONTROL INCLUDING ECONOMICS

2.1 GENERAL. A few of the many reasons to initiate a corrosion control program for a proposed or existing structure are:

- a. to insure continuity of operations for the success of the mission,
- b. to minimize hazard to life, limb, product or environment that a failure could cause,
- c. to satisfy government regulations,
- d. to minimize future expenditures resulting from material deterioration, thus minimizing annual operating costs.

The relative importance of these varies depending on the individual structure or system under consideration. Economics are not always the prime consideration.

2.2 CONTINUITY OF OPERATION. Military facilities are always maintained in a designated state of readiness; the activity's importance is determined by the assigned mission. For example, the loss of a fuel oil storage tank serving a boiler supplying heat to a housing area would not be vital to operations unless the same tank furnished fuel to a diesel electric generator set that supplied electric power to a communications center. Here, loss of the tank would be of vital military importance. It is, therefore, evident that the oil storage tank should be maintained in a high state of repair and protected from corrosion attack. Economics must often be sacrificed in order to preserve the continuous operation of vital facilities. Among the operations which may be considered vital are:

- Communication facilities
- Power facilities
- Air-craft fueling facilities
- Navigation aids
- Fire-fighting facilities
- Hospitals
- Missile-launching facilities
- Docks and piers
- Water supply systems

2.3 MINIMIZING HAZARDS. Certain materials used in military operations are hazardous to handle. Deterioration of the structures holding and servicing such materials may cause danger of fire and explosion, contamination of materials, injury to personnel, or damage to the environment. Corrosion deterioration of structures involving such hazards

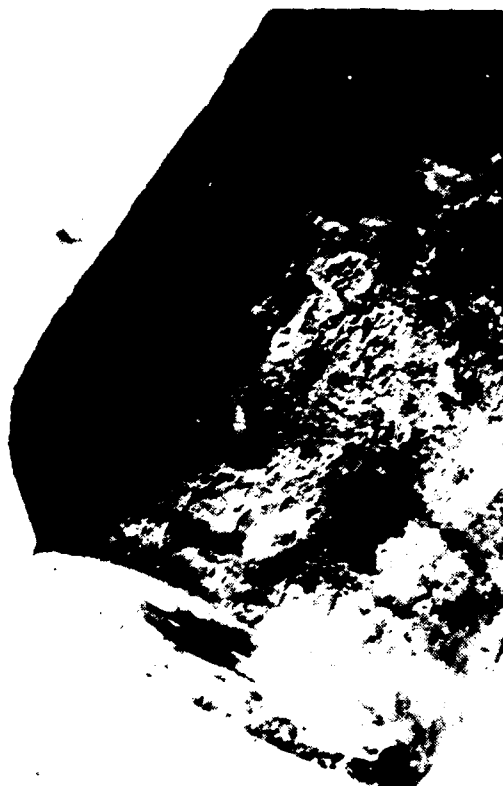


Figure 2-1
HYDRAULIC ELEVATOR CYLINDER
(SOIL CORROSION)

may cause damage far in excess of the economic value of the material contained or corroded structures; some of the possible damage - personal injury, pollution, depletion of natural resources - cannot be evaluated economically.

Many catastrophic structural failures have occurred in recent years, as in the past, due to improper, or lack of, corrosion control. Recently, a hydraulic elevator cylinder failure injured several people when the elevator fell 30 feet. Investigation revealed that soil corrosion of the elevator cylinder was the cause. The hydraulic cylinder extended 30 feet into the earth below basement floor level; corrosion deterioration took place on the bottom five inches. Only .096 inch of the .250 inch thick cylinder wall remained. This weakened the structure and the weld holding the 3/4 inch thick bottom bulkhead blew out, allowing the oil to escape from the cylinder rapidly. This caused the accident. Figure 2-1 illustrates the condition of the bottom of the cylinder. Soil conditions at the site favor buried steel corrosion.

Corrosion is a major cause of bridge failures. Recently several major highway bridges have collapsed under use as the result of corrosion. Serious property damage, injury, and loss of life occurred. Some failures were caused by deterioration of steel "H" piles, corroded in salt water. Bridge components are subject to corrosion deterioration from environmental conditions, galvanic cells and stray current action. Corrosion can be controlled through the use of coatings, cathodic protection, good specifications and the proper selection of materials for bridge construction.

Explosions are often caused by corrosion. Riveted boiler explosions have been known to result from stress corrosion or "caustic embrittlement". The use of welded pressure vessels has substantially reduced danger from these catastrophic failures. However, they still occur in some circumstances. Explosions have also caused damage and serious injury when gas leaks from pipeline corrosion failures. Corrosion of underground tanks at filling stations have resulted in explosions when gasoline leaked into sewage lines. Explosions are always a danger where fuels are handled or stored, but corrosion control can help to make many of them unnecessary.

These examples indicate that corrosion control may be necessary because of hazards even when it is not economically justifiable. Some of the facilities coming under this classification include:

- a. Pipelines handling gas, propane, and butane
- b. Buried tanks handling liquid and gaseous fuels
- c. Tanks and pipelines handling jet fuel and aviation gasoline
- d. Fuel oil pipelines and tanks
- e. Rocket-propellant storage facilities
- f. Hydraulic elevators and lifts.

2.4 GOVERNMENT REGULATIONS. The United States Department of Transportation has set minimum federal safety standards concerning corrosion control for the transportation of certain liquids and of natural and other gas by pipeline. These standards apply only to interstate and foreign commerce of hazardous liquids and to gas company distribution and transmission lines within the outer continental shelf. They are an excellent guideline for corrosion control of underground structures in general.

These regulations (Appendix B.) require the use of external coatings of good quality, the installation and inspection of cathodic protection systems, the installation of test leads for stray current control, and the proper application of electrical insulation where necessary. In addition, steps must be taken to mitigate internal corrosion of pipelines, and an evaluation of atmospheric corrosion of above-ground lines must be included in the test program.

In addition, State governments have set up local safety requirements which may be more rigid than federal standards. These regulations vary from state to state but also serve as a guideline to insure proper safety standards, even when they do not legally apply.

2.5 ECONOMIC CONSIDERATIONS. Once the three previously discussed considerations have been taken into account, the economics of corrosion control can be determined. In order to accomplish this, costs of corrosion losses must be compared to costs of the various methods of corrosion control.

The types of corrosion costs that must be considered include direct loss or metal structure damage as a result of corrosion, direct maintenance costs attributed to corrosion, increased construction costs resulting from overdesign to allow for corrosion losses, cost of lost product, downtime, and the costs of corrosion control.

The various methods of corrosion control, discussed in Section 5, include:

- a. selection of corrosion-resistant materials
- b. increased material thickness
- c. coatings and coverings
- d. cathodic protection
- e. anodic protection
- f. stray current control
- g. improved electrical grounding methods
- h. altering the metal's environment
- i. inhibitors

The value of any proposed corrosion control is determined by balancing installation, operating and maintenance costs of the program against costs attributable to corrosion without preventive measures.

2.5.1 Leak and Failure Records. A comparison of failure rates before and after corrosion mitigation provides a basis for economically justifying corrosion control. Each year's total corrosion failures are plotted cumulatively against time. If a logarithmic scale is used for cumulative failures, and a linear scale is used for time, a straight line curve results. This curve can be projected into the future. Figure 2-2 is an example, plotted for a large pipeline system. Here a "break" in the curve occurred after corrosion control (cathodic protection, in this case) was applied. Had no protection been employed, leaks would have continued along the original projected line. Instead, a sizable failure rate reduction resulted. It is important to note that cathodic protection and other means of corrosion control, applied to an existing system, do not replace metal already lost. If corrosion has proceeded to the point of deep pitting, some pits may continue to fail for several months. A year or so is required before beneficial effects can be seen.

Figure 2-3 shows how leak rates are used to compare several corrosion control methods. Here the leak rate for an 8-inch underground pipeline has been converted to dollars, and a linear scale is used. Several types of cathodic protection are examined here; but such a comparison would be equally valid for other control methods. This graph indicates also that a structure's service life is important in studying corrosion control economics. For the system illustrated in Figure 2-3, economics dictate no cathodic protection for a design service life of 10 years. For a 15-year life, deep anodes would be most economical and, for 25-years, a distributed impressed current groundbed would be chosen.

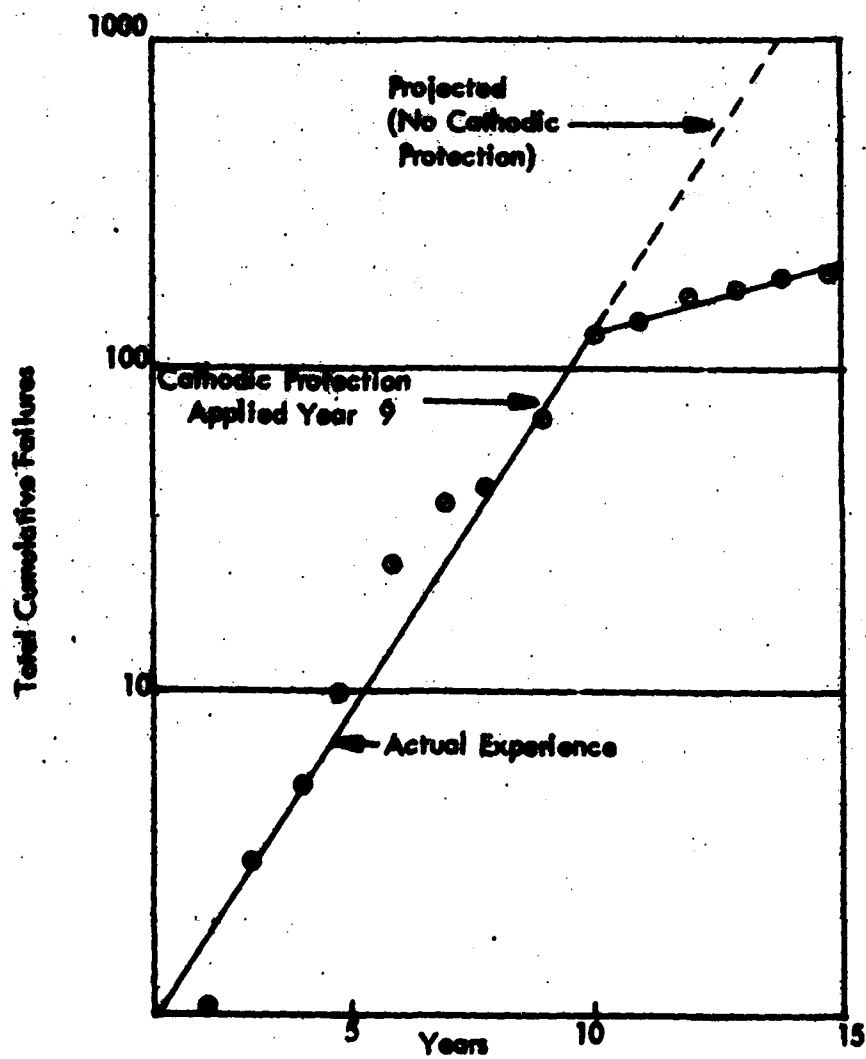


Figure 2-2
CORROSION FAILURE EXPECTANCY CURVE
(LARGE PIPELINE SYSTEM)

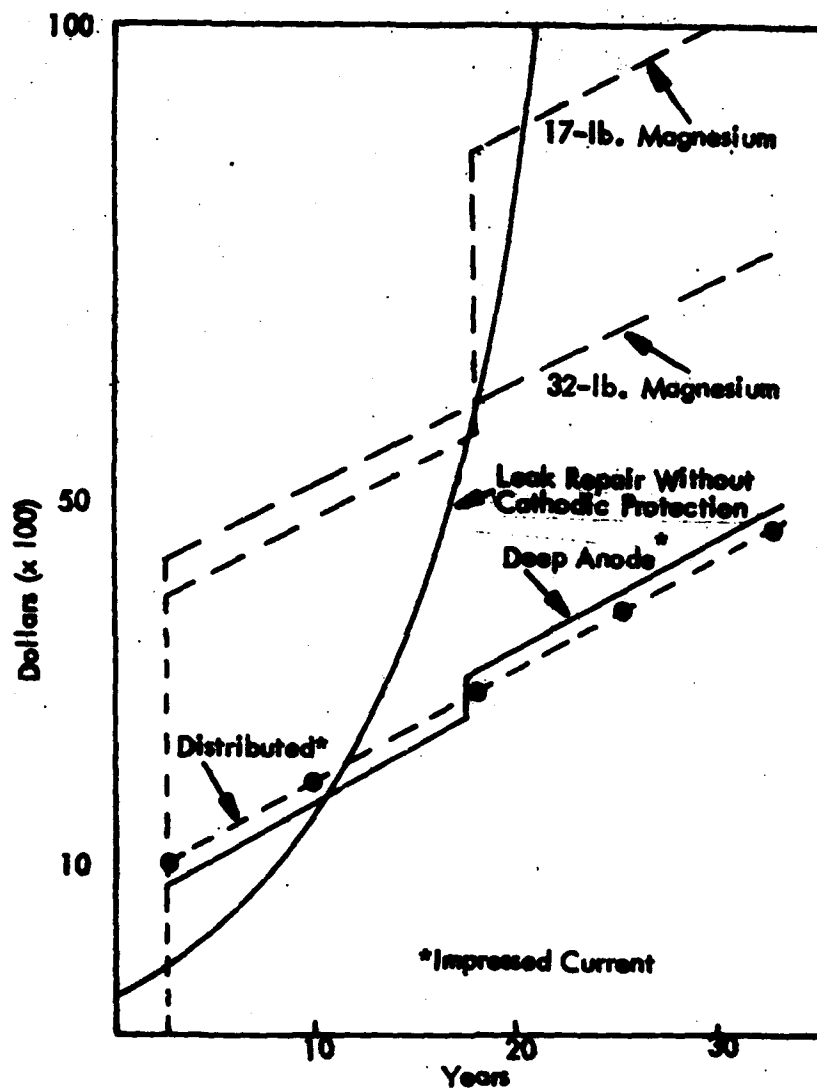


Figure 2-3
 COST COMPARISON OF CATHODIC PROTECTION
 vs. PIPELINE LEAK REPAIR
 (8-INCH PIPELINE)

2.5.2 Cost Analyses. Comparative corrosion and corrosion control costs are based on the relative capital investment and operating expenses required for various systems. Military methods employ a discounted cash flow technique for comparing relative capital and annual expenses. This type of analysis is discussed in detail in AFR 178-1 "Economic Analyses and Program Evaluation for Resource Management". The example given here illustrates the Present Value (discounting) technique described in this Regulation and is also based on methods outlined in NACE Standard RP-02-72.

In general, expenses for corrosion control for a military installation with a given expected life can be broken down into capital (those which occur only once or are different each year) and annual (those which are constant for a period of years) cash flows. Each cost is discounted using standard tables (see AFR 173-1) and a 10% discount rate. The discounted costs are then summed for the life of the installation and compared to determine the most favorable economic alternative.

Project design life for military installations must conform to the economic life schedule:

- (1) Utilities, Plants, and Utility Distribution Systems - 25 years.
- (2) Buildings - 25 years.
- (3) Operating Equipment - 10 years.

Underground and underwater corrosion systems generally fall in the first category.

It is important to remember that factors other than economics often play a most important role in determining the best of several alternatives. Safety, continuity of operation, and the other factors already discussed must always be considered first, before an economic analysis is made.

2.5.2.1 Cash Flow. Capital and annual cash flow and some of the various items to be considered are discussed here. All cost estimates are made without consideration of depreciation or inflation.

a. **Capital Cash Flow.** Capital expenditures and credits are considered at the time which they occur and are discounted accordingly. Initial investment, replacement costs, and salvage value are typical examples of capital cash flow. Initial investment occurs at year "0". Replacement costs may occur once, several times, or not at all during installation life. Salvage value is the estimate of installation worth at time of replacement or end of installation life.

b. **Annual Cash Flow.** Operating and maintenance costs are the generally considered annual expenses; these are estimated at a constant amount per year and discounted accordingly. Operating costs include such items as labor,

management, engineering and materials required on an annual basis for operations. Maintenance costs are those required to keep the facility in good operating order. These costs can be estimated on a yearly basis, excluding such things as major replacements which occur only every several years or so. Major replacements are considered under capital costs in the year(s) in which they are predicted to occur.

2.5.2.2 Illustration. The following example illustrates the method employed by the Military for comparative economic analysis. This example is based solely on economic considerations; in reality, the other justifications for corrosion control must also be analyzed.

An eight-mile, 6-inch diameter pipeline supplying a fluid to an Army installation is considered for four different operating conditions: cost of bare pipe, cost of bare pipe cathodically protected, cost of pipe protected with coal tar and felt wrap, and cost of pipe protected with coal tar, felt-wrapped, and supplemented with cathodic protection. It is further assumed that most of the pipe passes through low resistivity swamp land where the useful life of bare steel pipe is approximately 12.5 years due to the high corrosion rate. This example is intended to illustrate the method of economic analysis and not to imply that the method of corrosion control determined optimum for this installation is necessarily always the most economical.

a. Case 1: Bare pipe.

Based on: 12.5 year life, 25 year economic life. Total of 128 leaks in 25 years. Discount rate is 10%.

(1) Capital cash flow

	Cash Flow	Present Worth
(a) Cost of pipe, installed, year "0"	-\$440,000	-\$440,000
(b) Replacement cost, year 12.5	-\$440,000	-\$140,000
(c) Salvage value, years 12.5 or 25	0	0
Total Capital		-\$580,000

(2) Annual cash flow

	Cash Flow	Present Worth
(a) Leak repair and maintenance (\$200/leak)	-\$ 1,020	-\$ 9,300
(b) Average cost of product lost from leaks	-\$ 280	-\$ 2,500
Total Annual		-\$ 11,800

(3) Total Discounted Cash Flow - -\$591,800

- b. Case 2: Bare pipe, with cathodic protection.
Based on 25 year pipe life; 12.5 year
cathodic protection system life; 25 year
economic life. Total of 50 leaks in 25
years. Discount rate is 10%.

(1) Capital cash flow

	<u>Cash Flow</u>	<u>Present Worth</u>
(a) Cost of pipe installed, year 0.	-\$440,000	-\$440,000
(b) Cost of cathodic protection installed, year 0.	-\$ 50,000	-\$ 50,000
(c) Cathodic protection replacement, year 12.5.	-\$ 70,000	-\$ 22,300
(d) Salvage value of pipe, year 25.	0	0
(e) Salvage value of cathodic protection, years 12.5 or 25.	0	0

Total Capital

-\$512,300

(2) Annual cash flow

	<u>Cash Flow</u>	<u>Present Worth</u>
(a) Leak repair and maintenance	-\$ 400	-\$ 3,600
(b) Average cost of product lost from leaks	-\$ 110	-\$ 1,000
(c) Electrical power for rectifiers	-\$ 900	-\$ 8,200
(d) Other cathodic protection annual operating costs and maintenance	-\$ 2,500	-\$ 22,700

Total Annual

-\$ 35,500

(3) Total Discounted Cash Flow

-\$ 547,800

c. Case 3. Pipe coated with coal tar enamel and wrapped.

Based on 15 year coated pipe life, 25 year economic life. Total of 35 leaks in 25 years. Discount rate is 10%.

(1) Capital cash flow

	Cash Flow	Present Worth
(a) Cost of coated and wrapped pipe, installed, year 0.	-\$515,000	-\$515,000
(b) Replacement of pipe, year 15.	-\$515,000	-\$123,000
(c) Salvage value of pipe, year 25. (Straight-line depreciation)	+\$171,000	+\$ 15,800

Total Capital -\$622,200

(2) Annual cash flow

	Cash Flow	Present Worth
(a) Leak repair and maintenance	- \$ 300	-\$ 2,700
(b) Average cost of product	- \$ 77	-\$ 700
Total Annual		-\$ 3,400

(3) Total Discounted Cash Flow -\$625.600

- d. Case 4. Pipe, coated as in Case 3, with cathodic protection.
Based on 25 year pipe life, 25 year cathodic protection system life, 25 year economic life. Total of 15 leaks in 25 years. Discount rate is 10%.

(1) Capital cash flow

	Cash Flow	Present Worth
(a) Cost of coated and wrapped pipe, installed, year 0.	-\$515,000	-\$515,000
(b) Cost of cathodic protection installed, year 0.	-\$ 12,000	-\$ 12,000
(c) Salvage value of pipe, year 25.	0	0
(d) Salvage value of cathodic protection, year 25.	0	0
Total Capital		-\$527,000

(2) Annual cash flow

	Cash Flow	Present Worth
(a) Leak repair and	-\$ 130	-\$ 1,200
(b) Average cost of product lost from leaks	-\$ 30	-\$ 300
(c) Annual maintenance	-\$ 140	-\$ 1,300
(d) Electrical power for rectifiers	-\$ 100	-\$ 900
(e) Other cathodic protection-operating and maintenance	-\$ 500	-\$ 4,500
		-\$ 8,200
(3) <u>Total Discounted Cash Flow</u>		-\$535,200

e. Comparison of Results

	Total Cost
Case one	\$591,800
Case two	\$547,800
Case three	\$625,600
Case four	\$535,200

From this analysis we find that Case 4 is the most economical for the 25-year life required. Therefore, the pipe should be coated, wrapped, and cathodically protected.

SECTION 3 - CORROSION THEORY

3.1 CORROSION DEFINED. The National Association of Corrosion Engineers (NACE) has recently defined corrosion as:

"The deterioration of a material, usually a metal, because of a reaction with its environment."

Although many other definitions are available and acceptable, this is especially current, because it takes into account the increasing use of non-metals as materials of construction. Non-metals corrode, too, and will be considered along with the traditional subject of metallic corrosion.

Metallic corrosion is a natural phenomenon. Metals rarely occur in nature in their pure form, and corrosion is essentially the tendency of a refined metal to return to its natural state as an ore. Iron, for example, "rusts" to form the familiar iron oxide compound, one form of which is a main constituent of iron ore.

This tendency of metals to revert to their natural state is related to the release of energy originally stored up when metallic ore was refined to the pure metal. The metal stabilizes itself by releasing this energy and returning to its natural form, i.e. by corroding. The amount of energy released by this process and, hence, the inherent tendency to corrode is different for each metal. The relative tendency of various metals to corrode will be discussed later, in paragraph 3.4, covering the electromotive series.

3.2 ELECTROCHEMICAL ACTION. Electrochemical corrosion - a chemical reaction accompanied by D.C. electrical current flow - was traditionally taken to be the only form of corrosion. Metals, for the most part, corrode electrochemically, but a broader definition includes deterioration due at least in part to chemical or physical causes.

3.2.1 Ions and Ionization. A prerequisite of understanding the mechanism of electrochemical action is some knowledge of the structure of matter. Of particular interest are ions (electrically charged atoms or molecules) because the production of ions provides the means whereby a metal changes from a metallic form to a corroded form in an aqueous solution.

All matter is made up of atoms. Each atom, in turn, is made of a nucleus, which contains a given number of particles of unit positive charge (protons), surrounded by particles of unit negative charge (electrons) of like number. Each positive charge balances a negative charge so that the atom

itself is electrically neutral. For example, hydrogen, an element which plays an important part in many corrosion reactions, has only one proton in the nucleus and is associated with a single electron. The hydrogen atom, therefore, represents the simplest form of element construction. See Figure 3-1 and its explanation.

In more complex atoms, the charges are greater than one; but, in each case, the number of negatively charged electrons is equal to the number of positively charged protons in the nucleus. If one or more of these electrons are removed from any atom, the remaining electrons will not be sufficient to neutralize the positive charge in the nucleus, and the residual part of the atom, now called an ion, is positively charged. If one or more electrons are added to a neutral atom, a negatively charged ion results.

Molecules - groups of atoms bonded together and acting physically like an atom - form ions in the same way as atoms. In addition, molecules produce ions as a result of the process known as dissociation. Dissociation is merely the breaking up of a molecule into its component parts. When this occurs while the molecule is dissolved in water or other solvents, the component parts become ions, some of which carry positive charges and others, negative charges. To be more specific, there will always be in an aqueous solution positively charged hydrogen ions (H^+) and negatively charged hydroxyl ions (OH^-) as a result of the dissociation of water (H_2O). There may be, in addition, numerous other ions which are formed as a result of the dissociation of dissolved acids, bases, and salts. Acids dissociate into positively charged hydrogen ions and negatively charged ions of some nonmetallic atom or molecule. Hydrochloric acid (HCl), for example, dissociates into hydrogen ions (H^+) and chloride ions (Cl^-); sulfuric acid (H_2SO_4) dissociates into hydrogen ions (H^+) and sulfate ions (SO_4^{2-}). Bases or alkalies dissociate into positively charged ions of a metal or metal-like molecule and negatively charged hydroxyl ions.

For example, caustic soda or sodium hydroxide ($NaOH$) dissociates into sodium ions (Na^+) and hydroxyl ions (OH^-). It is to be noted that acids always yield hydrogen and that alkalies always yield hydroxyl ions. Salts, which are formed as a result of reactions between acids and bases, dissociate into ions of the nonmetallic atom or molecule which is characteristic of the acid and ions of the metal or metal-like molecule which is characteristic of the base. Common table salt, sodium chloride ($NaCl$), dissociates into sodium ions (Na^+) and chloride ions (Cl^-).

The formation of ions in solution is also a property of metals, although a mechanism different from dissociation applies.

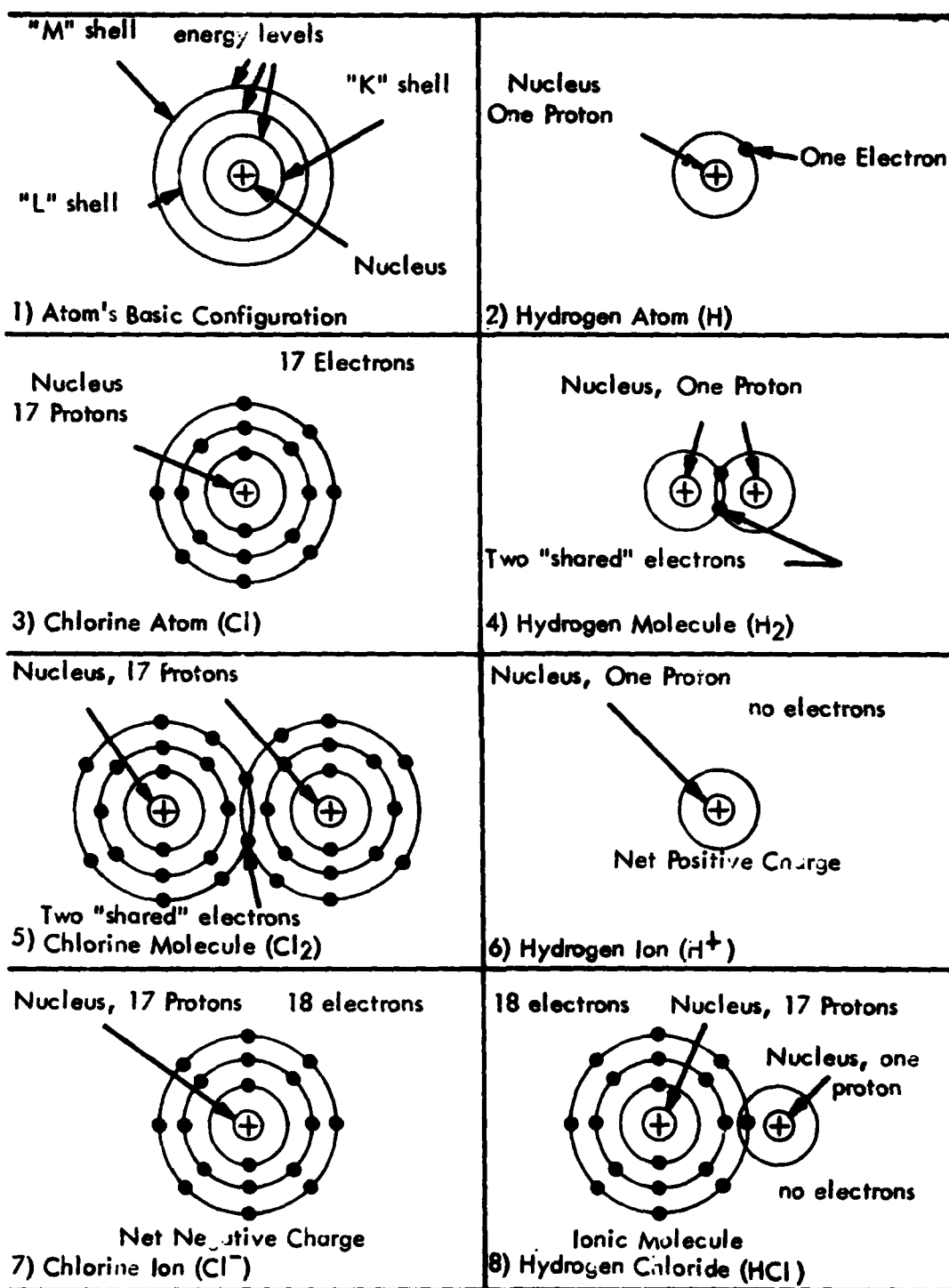


Figure 3-1
SCHEMATIC DIAGRAM OF ATOMS, MOLECULES, IONS

EXPLANATION OF FIGURE 3-1

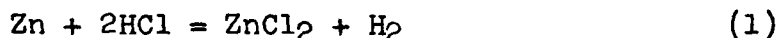
- 1) Each neutral atom contains a nucleus composed of "n" positive charges (protons) equal in number to the atomic weight and the same number of electrons. The electrons are negative charges dispersed in shells (energy levels) around the nucleus. Each shell contains no more than a characteristic maximum number of electrons. Shown here are the K (maximum 2 electrons), L (maximum 8 electrons), and M (maximum 8 electrons) shells. If all the shells of an atom contain these maximum numbers of electrons, the atom is relatively unreactive or "inert".
- 2) The hydrogen atom (H) consists of one electron in the K shell and a nucleus containing one proton.
- 3) The chlorine atom (Cl) is composed of a nucleus containing 17 protons surrounded by 17 electrons. The K shell contains 2 electrons; the L shell, 8 electrons; and the M shell, 7 electrons. The tendency of this atom is to gain an electron to "satisfy" its M shell.
- 4) The hydrogen molecule (H_2) consists of 2 hydrogen atoms whose electrons are "shared", forming a bond between the atoms.
- 5) The chlorine molecule (Cl_2) is composed of 2 chlorine atoms, sharing one electron from the M shell of each (2 electrons total). In this way, each atom has essentially 8 electrons (including the shared ones) in its outer M shell and is, therefore, satisfied.
- 6) The hydrogen ion (H^+) is a hydrogen atom without its electron. It is, therefore, positively charged.
- 7) The chlorine ion (Cl^-) is a chlorine atom with an extra electron in its M shell. There are 8 electrons in its M shell, and it is, therefore, satisfied. The chlorine ion has a net negative charge due to the additional electron.
- 8) Hydrogen Chloride (HCl , also known as hydrochloric acid) consists of a hydrogen ion and a chlorine ion, bonded together by their differences of charge (opposite charges attract). Hydrogen Chloride is an "ionic" compound, unlike the hydrogen and chlorine molecules which are referred to as "molecular" compounds because they share electrons.

Metal atoms are like other atoms in that they contain a nucleus of a given positive charge surrounded by a number of electrons totaling the same charge. However, according to the present concept, when metal atoms unite in one of the familiar metallic solids, the atoms do not remain neutral; positive ions are formed. These positive ions are bonded together by the electrons left over from the neutral metal atoms. No electron is held by any one ion; instead the electrons form a "cloud" of negative charge around the positive ions. The overall metal is electrically neutral; but ions form the basic structure, not atoms.

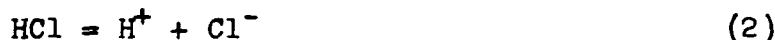
As a result of the unique structure of metals, when a metal dissolves in an aqueous solution, only positive ions result. One or more electrons are left behind on the parent metal. It is this process which takes place when a metal corrodes.

3.2.2 Oxidation-Reduction Reactions. Electrochemical reactions are made up of two parts - oxidation and reduction. Oxidation occurs when electrons are produced; reduction is indicated when electrons are consumed. In the overall reaction, the number of electrons produced always equals the number consumed; there is never an accumulation of electrons at any point.

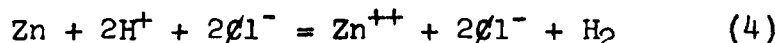
Consider the example of zinc metal (Zn) dissolving in hydrochloric acid (HCl). The reaction products of this electrochemical reaction are the soluble salt zinc chloride (ZnCl₂) and hydrogen gas (H₂). The overall reaction balanced chemically is written:



Note that electrons (e⁻) do not appear in this reaction. In order to determine the number of electrons transferred, the individual oxidation and reduction reactions are examined. First, the problem is simplified by realizing that both hydrochloric acid and zinc chloride dissociate in aqueous solution:



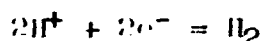
Substituting the ions for the molecules in reaction (1), one finds the chloride ions "cancel out", playing no important part in the reaction:



Now the oxidation reaction is seen to be zinc metal dissolving to zinc ions and electrons:



The reduction reaction then unites hydrogen ions and electrons to produce hydrogen gas:



For every zinc atom dissolved, one hydrogen molecule is produced and two electrons are transferred. Complicated reactions involving many chemical species, also occur, but any electrochemical reaction always contains oxidation and reduction.

3.2.3 The Corrosion Cell. Because metals corrode electrochemically, the corrosion process can be divided into oxidation and reduction reactions. These reactions take place at different points connected together electrically to allow the electrons produced at one point to be consumed at the other. This entire electrical circuit is the corrosion cell.

3.2.3.1 Description. The corrosion cell is made up of four basic parts: anode, cathode, electrolyte, and external electrical path. The oxidation reaction (corrosion) takes place at the anode; reduction occurs at the cathode. Electrons flow from anode to cathode in the external electrical path. The electrolyte, a fluid or solid in which ions move freely, completes the circuit. In order for corrosion of a metal to occur, all four parts must be present.

Again consider the example of zinc metal dissolving in hydrochloric acid, this time in somewhat different form (Figure 3-2). The zinc metal strip is the anode; the platinum strip, the cathode. The wire connecting the two metals is the external electrical path, and the hydrochloric acid, in which the two metals are partially submerged, is the electrolyte. Oxidation occurs at the zinc anode. Zinc ions go into solution and electrons travel through the external wire path to the platinum cathode. Here reduction occurs as the electrons on the cathode surface combine with the hydrogen ions in the electrolyte to form hydrogen gas. In the electrolyte there is a net motion of positive ions toward the cathode and negative ions, toward the anode. As before, one zinc ion is produced (at the anode) for each molecule of hydrogen gas produced (at the cathode).

Moving charges, whether electrons or ions, constitute an electrical current. By Ohm's law, a voltage or potential gradient causes a current flow. A potential gradient in a metal causes electron transfer. A potential gradient in an electrolyte causes ion transfer. By definition, current flow is in the direction positive charges move; that, is, opposite the direction of electron or negative ion flow. It is the potential gradient between the anode and cathode that results in current flow in a corrosion cell.

3.2.3.2 Electrolytes. The electrolyte in a corrosion cell differs from the three metallic parts, because electrons do not use it as a path. Instead, ions are the charge carriers.

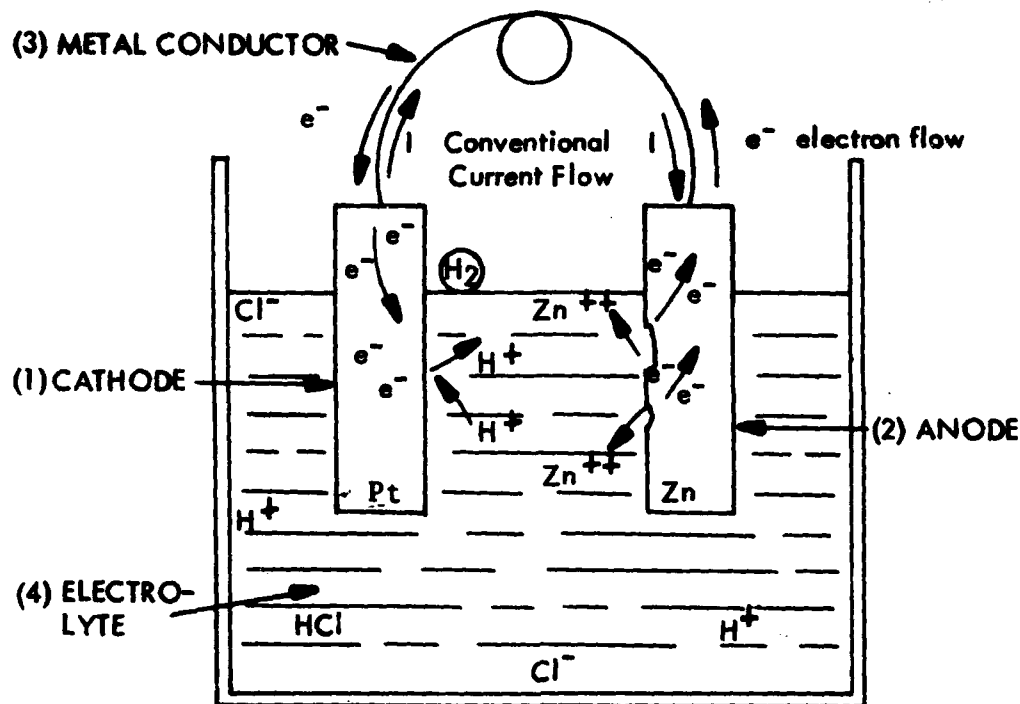


Figure 3-2
THE BASIC CORROSION CELL

a. Importance of Electrolytes. An electrolyte is a substance such as water or soil which serves as a medium for the flow of an electric current between anode and cathode areas of an active corrosion cell. Corrosion of metals cannot take place except in the presence of a suitable electrolyte. Electrolytes are, therefore, important and should be better understood in order to comprehend the process of corrosion.

The conductivity of an electrolyte depends upon the presence of ions. When the total number of positive charges in an electrolyte is equal to the total number of negative charges, the electrolyte is considered to be in a state of equilibrium. Now, if metal ions from a corroding metal such as zinc (Zn⁺⁺) go into solution, the electrochemical neutrality of the electrolyte becomes unbalanced because an equal number of negatively charged ions are not added at the same time. In order to restore the balance, it is necessary to do one of two things: either add an equivalent number of

negatively charged ions to match the zinc ions (Zn^{++}), or an equal number of positive charges must be displaced from the solution (electrolyte). It is the latter which is considered here, because it is the one which is encountered in electrochemical corrosion reactions. The ions displaced may be those of another metal but, in most cases, it is the element hydrogen combined to form hydrogen gas.

The ability of an electrolyte to oppose the flow of electric current is expressed in corrosion terminology as the electrical resistivity of an electrolyte. It is usually computed in ohms resistance for 1 square centimeter of cross section and 1 centimeter length of the electrolyte. The resistivity of the electrolyte is commonly expressed as ohm-cm., and will be used in this form throughout the text. A low resistivity indicates that the electrolyte is a good conductor of electricity, whereas a high resistivity indicates that the electrolyte is a poor conductor of electricity.

b. Soil as an Electrolyte.

(1) Characteristics. Soils vary widely in physical and chemical characteristics which in turn affect their corrosivity towards metals. The Department of Agriculture recognizes several soil groups, which are divided into some three thousand soil series, most of which have at least three horizons or layers, differing in physical and chemical properties. The name of a soil is divided into two parts: the first indicating the series to which the soil belongs, and the second, the texture of the uppermost soil layer. The texture of the upper layer is determined by the percentage of various size particles. The size particles in soils are classified as those having diameters of two or more millimeters and those having diameters of less than two millimeters, such as clay and silt. In general, the term soil is applied to the first few feet of finely divided material on the surface of earth which at one time was solid rock. Soils consist essentially of four types of substances: mineral matter, organic matter, water, and air.

(2) Effect of Moisture. The moisture content of a soil greatly affects its corrosivity. This is due to the decrease in the resistivity with the increase in moisture content up to a point near saturation. It should be remembered that it is the ion content of the electrolyte that determines the resistance to the flow of an electric current. The graph in Figure 3-3 illustrates the change in resistivity with the change in moisture of a specific clay soil. With only 5 percent moisture, the resistivity was 1,200,000 ohm-cm. and with a moisture content near 20 percent, the resistivity dropped to 5000 ohm-cm. Any increase in moisture content beyond 20 percent did not appreciably affect the resistivity.

Other types of soils yield similar curves but the lowest resistivity point may vary depending on the constituent salts.

(3) Effect of Aeration. In well-aerated soils, the iron compounds are oxidized to the ferric state $\text{Fe}(\text{OH})_3$. These soils have a red or yellow color. In poorly aerated soils, due to the low oxygen content, the soils are generally gray in color, indicating the presence of reduced forms of iron.

Size of soil particles has a definite relation to aeration and ability of soils to retain moisture. Difference in size of soil particles may cause the formation of concentration cells. Metals in well-aerated soils (larger soil particles) will be cathodic to metals in poorly-aerated soils (finer soil particles). (paragraph 4.3.2.).

Aeration factors are those that affect the access of oxygen and moisture to the metal and thereby affect the corrosion. Oxygen can be from either atmospheric sources or from the reduction of salts or compounds. This oxygen may tend to stimulate or retard the corrosion process, the quantity being the controlling factor. Oxygen when present in large quantities will form insoluble compounds at the anode and thus retard corrosion. Oxygen, when present in ordinary quantities, stimulates the corrosion process by combining with hydrogen at the cathode. In ordinary quantities, oxygen may also combine with metal ions which have migrated away from the anode. This combination further increases the rate of corrosion. Oxygen, when present in small quantities or absent, will not affect the corrosion process and

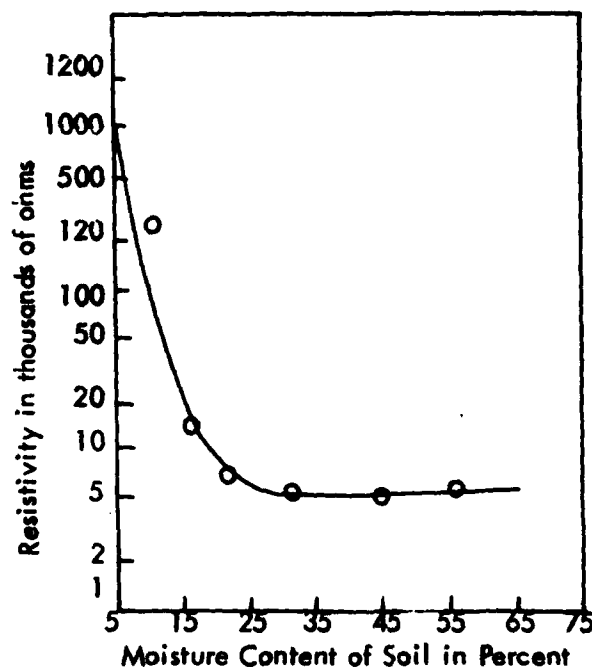


Figure 3-3
EFFECT OF MOISTURE CONTENT
ON RESISTIVITY OF A CLAY SOIL

corrosion will proceed at a minimum rate. Some specific examples illustrate the effects of well-aerated and poorly-aerated soils.

(a) On tanks or pipelines, the upper portion of the structure usually is in well-aerated soil, whereas the lower portion is in poorly-aerated soil. This causes the bottom of the structure to corrode due to the formation of a differential oxygen cell with the anode on the bottom (paragraph 4.3.2).

(b) In cross-country pipelines, a different type aeration cell is formed. Soils in the open are more aerated than in compacted areas as highway and railroad beds. Pipelines exposed to such variations will generally corrode more readily under compacted areas because of the difference in aeration.

(4) Soil Classification. Soils are classified according to physical and chemical characteristics rather than from their geologic origin or geographic location. There are two general classifications in the United States, those in which lime accumulates in the subsoil and those in which it does not. The lime-forming soils lie west of a line from northwestern Minnesota to a point on the Gulf of Mexico 100 miles north of the Mexican border. East of this line the non-lime-forming soils predominate. For further information, see reference 1.

Soils can further be classified into resistivity ranges in ohm-cm., such as shown in Table 3-1. The corrosion activity indicated in this chart excludes such factors as stray current or galvanic cells which could change the values.

Table 3-1

<u>Resistivity Classification</u>	<u>Resistivity Range ohm-cm.</u>	<u>Anticipated Corrosion Activity</u>
Low	0 to 2,000	Severe
Medium	2,000 to 10,000	Moderate
High	10,000 to 30,000	Mild
Very High	Over 30,000	Unlikely.

c. Water as an Electrolyte.

(1) Fresh Water

(a) Effect of Dissolved Solids. The most frequent contact with dissolved solids is that found in natural waters. Water in nature is never really pure. Even when it falls from the clouds in its purest natural state, it contains some dissolved dust and gases, plus suspended matter. After it has run over the surface of the ground or percolated through soil or rock layers, its impurities have greatly

increased because water is practically a universal solvent and dissolves a little of everything it touches.

In natural fresh water, the relative average order of occurrence of alkaline minerals is calcium, sodium, magnesium, and potassium. Silica is a constituent of all natural waters. In surface waters, it ranges from less than 2 parts per million to over 60 parts per million. In ground waters, it ranges from about 2 parts per million to about 110 parts per million. These figures are for domestic waters. Highly mineralized waters have a higher silica content. Silica makes water harmful and dangerous to steam boilers, since it precipitates and forms a hard, glassy coating on inside surfaces.

Water hardness refers to the content of salts of calcium and magnesium. It is usually expressed as an equivalent concentration of calcium carbonate and may vary from 10 to 1800 parts per million. Hardness is generally considered objectionable, since it forms scale and interferes with dyes and soaps. However, in some water-treatment plants, calcium and magnesium salts are added to water to control internal corrosion.

(b) Effect of Dissolved Gases. Sources of natural water are wells, springs, ponds, and the like, all depending on rain water. As rain falls through the air, each drop absorbs gases, and additional gases are absorbed as the water passes through streams, rivers, and waterfalls on its way to the sea. The most significant of these gases are oxygen, carbon dioxide, and hydrogen sulfide.

Oxygen is an extremely active element, attacking some metals strongly. Oxygen also acts as a cathodic depolarizer by precipitating metal ions out of solution, permitting more metal ions to enter into solution and also by combining with hydrogen films on metal surfaces, thereby exposing the metal to direct contact with water. One of the most vulnerable structural metals is steel. In the presence of free oxygen, a film of reddish brown ferric oxide quickly forms. This is the familiar "rust" that everyone has observed. Rust on the inside of water pipes is apt to flake off, which leaves fresh metal exposed to attack by oxygen and also leads to clogging of the pipe where the rust flakes may accumulate. This corrosion is proportional to the dissolved oxygen content and also to the temperature.

Hydrogen sulfide gases are also found in some water that is distasteful for drinking purposes; they are corrosive to most metals and are objectionable for this reason. Free carbon dioxide gas is also found in most natural waters. In surface waters, the content is usually low. In some rivers it can at times reach 50 parts per million. In

ground waters, carbon dioxide ranges from zero to concentrations so high that they cause the water to bubble when the pressure is released. Waters derive their carbon dioxide content from various sources. Carbon dioxide is also formed when bicarbonates are decomposed.

Carbon dioxide, associated with oxygen, can cause serious corrosion in a boiler. It either enters the system as free carbon dioxide gas in the raw make-up water or is generated in the boiler by the decomposition of carbonates and bicarbonates of sodium, calcium, and magnesium.

(c) The pH Range. Natural waters found in soils and rivers usually range in pH from six to eight.

(d) Resistivity Range. The resistivity of naturally fresh water usually varies from 300 to 20,000 ohm-cm.

(2) Sea Water. Sea water is characterized by the presence of dissolved salts, principally sodium chloride. Since most of these salts are chemically neutral, the pH of salt water is in about the same range as that of fresh water, but is most often greater than 7. Resistivity, however, is different. It may be as low as 15 ohm-cm. in tropical waters or as high as 40 ohm-cm. These low values offer little resistance to the flow of electric currents; therefore, sea water is conducive to corrosion.

3.2.3.3 Anodic and Cathodic Processes. The example of a corrosion cell, given earlier, indicated three distinct pieces of metal (zinc, platinum, and connecting wire) as the anode, cathode and electrical path. However, it would have been equally correct to show one piece of metal, containing all three parts of the cell. A piece of iron, in low resistivity soil for example, corrodes even when not in contact with other metals. Here, certain well-defined areas (anodic and cathodic) exist on the surface of the metal. At the anodic areas, metal goes into solution as positive ions; at the cathodic areas, a reducing action takes place which usually does not involve the metal. The remainder of the metal acts as the path for electron transfer. The four distinct parts of the cell still exist, but three of them are located on the same piece of metal.

The reason for a corrosion cell's existence on a single piece of metal in an electrolyte is the same as for a bi-metal corrosion cell - a voltage or potential difference exists between anode and cathode causing electrical charge to move. If there were no potential difference between the two electrodes, no anode and cathode areas would exist; hence, no corrosion. This can be explained in terms of solution pressure and osmotic pressure.

Each metal has a definite solution pressure. This is the measure of the tendency of the metal to pass into aqueous solution in the form of ions. It is opposed by the osmotic pressure of metal ions, which tends to drive them out of solution and deposit them on the metal. When a metal is immersed in an aqueous solution of one of its salts, solution potential of the metal (P) tends to increase the number of ions in the solution. On the other hand, the osmotic pressure of the ions (p) tends to decrease the number of ions. With an active metal such as zinc, (P) is greater than (p). Under this condition, positively charged ions go into solution and electrons are produced. When the solution pressure equals the osmotic pressure, no further ionic change will occur and no potential is developed. When (p) is greater than (P) as in the case of copper and the more noble metals in a solution of their salts, ions of the metal are deposited, consuming electrons. The solution in the vicinity of the electrode becomes charged by the corresponding negative ions.

a. Area Effect. Corrosion of a metal takes place where current leaves the surface and enters into the electrolyte. Total current leaving the anode surface exactly equals the total current entering the cathode surface. Thus, for a given cathode area and amount of current, any size anode of a certain metal will lose the same weight of metal to corrosion. Also, the larger the cathode-to-anode area ratio, the greater the corrosion per unit area of anode. This concept, very important in corrosion control, is the area effect. It implies that the smaller the anode, the higher the corrosion rate.

b. Electrochemical Equivalents. Dissimilar metals, when coupled together in a suitable environment, will corrode according to Faraday's law; that is, it requires 96,500 coulombs or 26.8 ampere-hours to remove 1 gram-equivalent of the metal. At this rate, the amount of metal removed by a current of 1 ampere flowing for one year is shown on Table 3-2.

Table 3-2

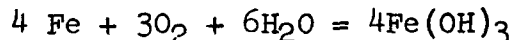
Electrochemical Equivalents of Some of the Common Metals

<u>Metals</u>	<u>Pounds Loss per Amp-Year</u>
Iron (Fe ⁺⁺)	20.1
Aluminum (Al ⁺⁺⁺)	6.5
Lead (Pb ⁺⁺)	74.5
Copper (Cu ⁺⁺)	22.8
Zinc (Zn ⁺⁺)	23.6
Magnesium (Mg ⁺⁺)	8.8
Nickel (Ni ⁺⁺)	21.1
Tin (Sn ⁺⁺)	42.0
Silver (Ag ⁺)	77.6
Carbon (C ⁺⁺⁺)	2.2

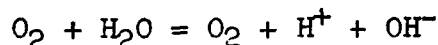
c. Some Typical Reactions. The example of zinc corroding in acid solution and producing hydrogen is a simplified situation. Often, several reactions occur at the cathode, while at the anode, metal ions form corrosion products instead of merely dissolving.

Iron (Fe) forming rust (Fe(OH)₃) in water (H₂O) containing dissolved oxygen (O₂) may involve a number of reactions.

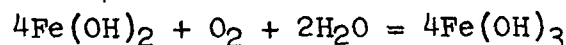
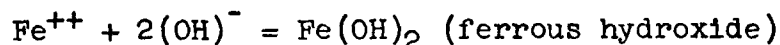
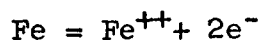
(1) Overall reaction



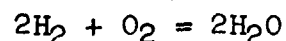
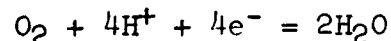
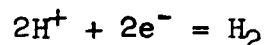
(2) Electrolyse dissociation



(3) Anode reactions

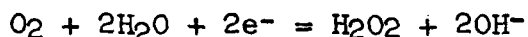


(4) Cathode reactions



Additional reactions take place, particularly in the presence of sufficient oxygen. Oxygen promotes corrosion by converting ferrous iron to the less soluble ferric iron (rust). This rust may form away from or next to the iron surface, depending on several factors including alkalinity and oxygen content. When the rust film forms on the iron surface, it becomes cathodic to an unruined metal surface; the unruined surface becomes anodic and goes into solution. Thus, the oxygen content of any solution is an important factor in the rate of corrosion. In the absence of oxygen or some oxidizing agent (agent which behaves as oxygen in removing electrons from an element), corrosion may cease.

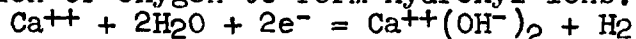
Some other positive ions, which take part in reactions at the cathode, are calcium and magnesium. They form bases, resulting in an alkaline condition at the cathode. Under certain conditions, these bases may be present in concentrations high enough to allow their precipitation.



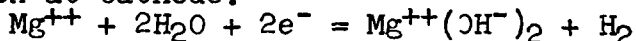
Reduction of oxygen to form hydrogen peroxide and hydroxyl ions.



Reduction of oxygen to form hydroxyl ions.



Reaction at cathode.



Reaction at cathode.

3.3 FACTORS AFFECTING CORROSION. The potential difference between the anode and cathode can originate from several sources. Almost any chemical or physical difference between the anode and cathode areas will cause a natural potential difference. This difference can be in the electrolyte or the metal. Common differences which cause potentials sufficient to support substantial corrosion are different metals (for example, copper and iron coupled will have a potential difference of approximately 0.6 volt), impurities in the metal, different metal surface conditions, different concentrations of chemicals within the electrolyte (especially oxygen concentration), and temperature differentials. Any direct electric current, such as stray currents from improperly grounded D.C. motors or generators, will support corrosion. Usually alternating current will not cause appreciable corrosion when leaving a metal structure unless the current is partially rectified. Because of the large voltages and amperages usually involved, stray currents can cause unbelievably extensive and rapid corrosion.

It is important to remember that this corrosion process is universal for all metals. Cast iron, steel, copper, lead, concrete reinforcing steel, stainless steels, exotic metals -

all will corrode given a favorable environment. For the common metals, such as cast iron and structural steel, most environments are corrosive. Some factors which generally effect corrosion of metals are discussed here.

3.3.1 Electrolyte Resistivity. The effects of various factors on soil and water resistivity have been previously discussed. The effect of electrolyte resistivity, in general, is quite simple; as resistivity decreases, corrosion increases.

3.3.2 Temperature. Temperature may alter the corrosion behavior of an electrolyte or a metal, with different results, depending on the system being considered. In general, it is known that chemical reactions usually are more rapid at elevated temperatures; this idea applies to reactions that make up the corrosion process, too. It does not always hold true, of course; often combinations of factors result in unexpected behavior at high temperature. For example, galvanized steel is a common material of construction; it is known that below about 140°F, the zinc galvanizing is anodic to the steel base and corrodes preferentially, protecting the steel. At elevated temperatures (above about 170°F), however, this situation is reversed, as the steel becomes anodic to the zinc and actually corrodes the metal it was designed to protect.

Some general comments about the effects of temperature on the behavior of the common electrolytes, soil and water, may be safely made.

The effect of temperature on the resistivity of soil is a gradual increase in resistivity with a decrease in temperature until the freezing point is reached. At temperatures below the freezing point, the resistance increases rapidly according to the formula:

$$R_{15.5} = \frac{R_t(24.5 + t)}{40}$$

where

$R_{15.5}$ = resistance of the soil at 15.5°C (60°F)

R_t = observed resistance at temperature $t^\circ\text{C}$.

The relation between soil resistance and temperature is shown in Figure 3-4.

Temperature also affects the corrosive powers of dissolved oxygen in fresh water. Laboratory tests indicate that an increase in temperature from 140° to 194°F. doubles the rate of corrosion by oxygen in water.

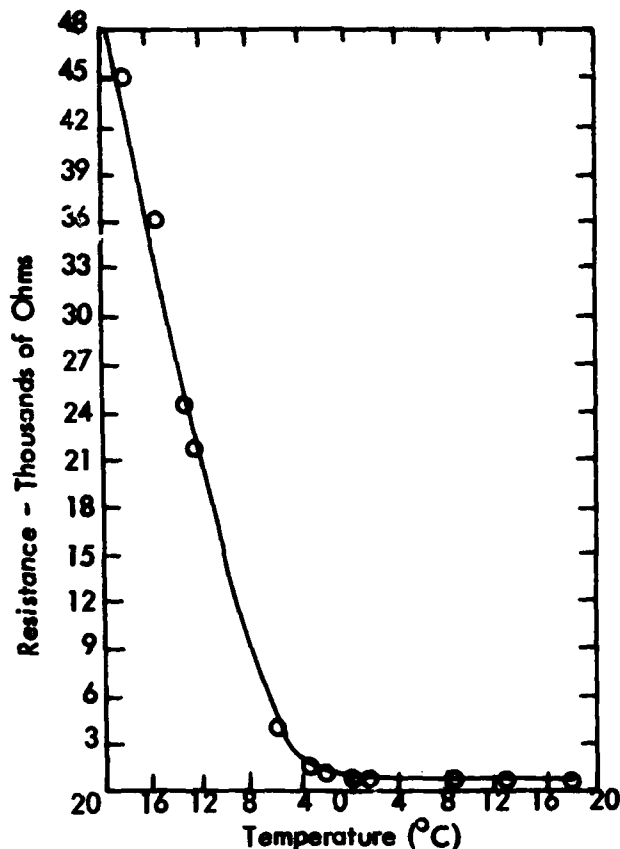


Figure 3-4
EFFECT OF TEMPERATURE ON SOIL RESISTIVITY

3.3.3 pH

3.3.3.1 The Meaning of pH. In an aqueous solution there are always some hydrogen ions and some hydroxyl ions as a result of dissociation of water. The relative amounts of these two ions determine whether any solution has the familiar sour taste, the ability to turn blue litmus paper red, and other acid characteristics; or whether it has a bitter taste, soapy feel, the ability to turn red litmus paper blue, and other alkaline characteristics; or whether it is chemically neutral, neither alkaline nor acid. If hydrogen ions are in excess, the solution reacts as an acid; if hydroxyl ions are in excess, the solution reacts as an alkali; and if both ions are present in equal amounts, the solution is neutral. Going further, acids are identified as substances which, when dissolved in water, increase hydrogen ion concentration, and alkalis as those substances which, when dissolved in water, increase hydroxyl ion concentration.

An important feature of the behavior of any solution containing hydrogen ions (H^+) and hydroxyl ions (OH^-) is that while concentration of individual ions may vary over a wide range, the product of these concentrations is about constant. It follows, then, that if concentration of one ion is increased, concentration of the other is automatically decreased to a corresponding extent. The constant for pure water has been evaluated and found to be approximately 10^{-14} . Since this represents the product of equal concentration of hydrogen ions (H^+) and hydroxyl ions (OH^-), concentration of each ion must be 10^{-7} gram-ions per liter.

Since the sum of the exponents (the product of the concentrations) is a constant value, it follows that if it is possible to measure the concentration of either ion, the other can be calculated. Satisfactory methods have been developed to measure the concentration of hydrogen ions, and it has become common practice to state both hydrogen and hydroxyl ion concentrations in terms of hydrogen ion concentration only.

Since it is customary to state ion concentration of a solution only in its H value, simple numbers which are logarithms of the reciprocals of the corresponding hydrogen ion concentration are substituted for concentrations. These simple numbers are called pH values. The following should be remembered: a pH value of 7.0 indicates a balance between H^+ and OH^- ions and the solution is said to be neutral; pH values of less than 7.0 indicate an acid solution with hydrogen ion concentration becoming progressively greater as the numerical value of pH becomes smaller; the pH values greater than 7.0 indicate an alkaline solution with the hydroxyl ion concentration becoming progressively greater and the hydrogen ion concentration smaller as the numerical value of pH becomes larger, and a variation of one pH unit indicates a tenfold variation in the ionic concentrations. For example, a solution having a pH value of 6.0 has ten times more hydrogen ions and one-tenth as many hydroxyl ions as another solution having a pH value of 7.0.

3.3.3.2 Effect of pH on Corrosion. The effect of pH, like temperature, depends greatly on the system under consideration. For many systems, little or no effects are observed over a wide range of pH; other systems behave differently at opposite ends of the scale.

Amphoteric metals exhibit both acid and alkaline properties depending on their environment. Examples are zinc, lead, and aluminum. Amphoteric metals are subject to increased corrosion in either basic or acidic electrolytes; consequently, their use is restricted to near-neutral pH systems.

Iron is not amphoteric. The effect of water on corrosion of iron at 72° and 104°F is shown in Figure 3-5. Specimens of mild steel were exposed to water containing an average of 5 milliliters of oxygen per liter. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were added to produce the alkaline and acid ranges of pH, respectively.

At pH values greater than needed for hydrogen evaluation (pH = 4), results of Figure 3-5 can be explained by the protective layer of hydrous ferrous oxide which is formed on the iron surface by the initial corrosion reaction. Regardless of the actual pH of water between pH 4 and 9.5, the surface of the iron is always in contact with an alkaline saturated solution of hydrous ferrous oxide.

Corrosion continues as rapidly as oxygen can diffuse through the protective layer, the layer being continually renewed by the corrosion process. Since the corrosion product film next to the iron is essentially unchanged by external conditions within the above range of pH, corrosion rate is not altered except by change in dissolved oxygen. At pH 9.5 (72°F.), however, further increase in alkalinity extends its effect to the iron surface and either decreases the surface reaction rate (the iron becomes passive) or decreases permeability of the corrosion product layer to oxygen (by decreasing the solubility of the ferrous ion, Fe^{++}). In either instance the corrosion rate is expected to decrease as is observed.

Within the acid region (pH is less than 4), on the other hand, the alkaline corrosion product layer is dissolved and the acid reacts directly with iron. For acids that are not totally dissociated into their component ions (weak acids), the pH at which hydrogen is evolved will shift to a higher (less acid) value. For example, carbonic acid at room temperatures causes hydrogen evolution at a pH of 6 and phenol solutions at a pH of 7; whereas with sulfuric or hydrochloric acid, the value of pH must reach 4. It appears that total acidity rather than pH of an acid is the controlling factor.

3.3.4 Pressure. Usually, pressure is constant enough to be ignored as a factor in corrosion. However, in some industrial applications, it may be important. Pressure sometimes does have an effect on chemical reactions and may need to be considered in extreme cases.

3.3.5 Radiation. The effects of radiation on corrosion are not very clear. In general, it is known that such properties of metals and other materials as yield strength and percent elongation are altered by radiation. Beyond this point, little is known.

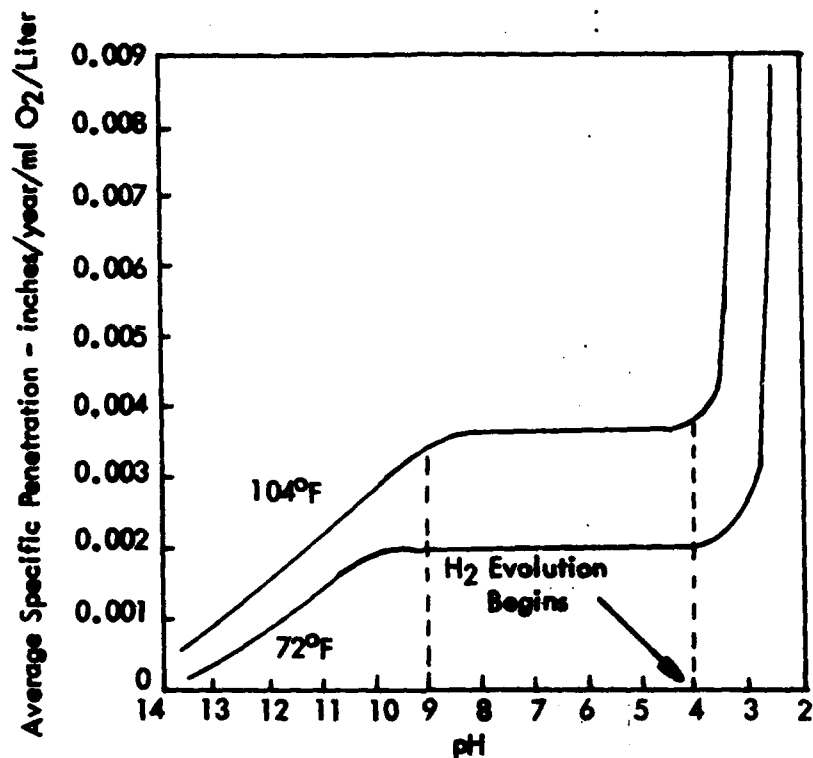


Figure 3-5

EFFECT OF pH ON CORROSION OF MILD STEEL

3.3.6 Metallurgical Factors. The metallurgical history of a metal can often reveal much about its tendency to corrode. Some knowledge of basic metallurgy is, therefore, necessary for a complete understanding of corrosion.

3.3.6.1 Structure of Metals. As noted earlier, metallic solids consist of positive ions bonded together in a cloud of electrons. All of the ions share all of the electrons, resulting in relatively unrestricted movement of the

electrons. This free movement, restricted only by collisions with other electrons, accounts for the electrical and thermal conductivity exhibited by metallic solids. The collisions account for resistivity. Within the solid, the ions are arranged in a pattern, distinctive of the substance in question. This pattern is called the space lattice, and it is characterized by an orderly, repetitive arrangement of the ions to allow as close packing as possible. A variety of lattice forms are possible, but metals usually exhibit cubic, hexagonal, or tetragonal lattices.

A regular combination of lattices, few or many, is called a crystal. Crystals form naturally when the metal cools from its liquid state; many crystals start to form simultaneously at different points in the random distribution of atoms or molecules which constitutes a liquid. These crystals enlarge along their planes of growth until they contact other crystals. Along the lines of contact irregular boundaries form, and the resulting irregular crystals are referred to as grains. Metallic grains normally vary in diameter from 0.01 to 0.001 inch. The precise size, shape, and orientation of the grains depend upon the rate at which the metal cools, and these things help determine the properties of the solid.

This microstructure of the metal may be altered by alloying (adding or substituting other substances into the space lattice), heat treatment (melting and reforming of the grains), or mechanical deformation. Any of these processes singly or together can greatly affect the corrosion properties of a metal.

3.3.6.2 Alloying. Metals in the pure form are rare in engineering applications. Generally, alloys - combinations of substances which together act like metals - are the materials employed, because they can be altered to produce a wide range of properties.

Alloys may be solid solutions of the elements involved, or mechanical mixtures, or compounds. Whatever the method of formation, alloys exhibit properties entirely their own.

The corrosion properties of alloys depend on many factors including the substances involved, the relative amounts, and the method of alloying. Properties of individual alloys are discussed in paragraph 5.3.

3.3.6.3 Heat Treatment. In general, heat treatment is the heating and cooling of a metallic solid to obtain certain desirable properties. As mentioned above, heat treatment can be used to change the size and orientation of

grains which can alter the properties. Heat treating can also change the chemical composition of alloys by removing inhomogeneities initiated by rapid cooling.

a. Annealing to Reduce Stress. When a metal has been mechanically deformed by a process such as cold-rolling, forging, etc., high residual stresses are produced. In a metal which has cooled unevenly, residual stresses also exist, usually to a lesser degree. The grains can be made more uniform and the stresses relieved by annealing. Annealing of stressed metals includes three stages: recovery, recrystallization, and grain growth.

(1) Recovery. Recovery of a cold worked metal is often used as a partial anneal, because in it the metal regains some ductility without losing much of the high strength it gained in cold work. Such a process often produces improved corrosion resistance and toughness.

(2) Recrystallization. In recrystallization of a cold worked metal, new grains form at the boundaries of the existing grains and gradually replace them. These new grains are stress free and are accompanied by the return of strength properties to their low pre-deformation state and an increase in ductility.

(3) Grain Growth. The third step, grain growth, merely produces further growth in grain size including the elimination of some grains as others grow. This process must be controlled, so that a large-grained, unmachinable metal does not result.

b. Annealing to Homogenize. Coring (chemical inhomogeneity) is often a problem in cast metals because of uneven cooling. Coring reduces corrosion resistance of many metals and also decreases mechanical properties. The specific treatment greatly depends on the alloy under consideration, but the basis for homogenization annealing is diffusion. By heating the metal, the atoms are allowed to move to their more natural homogeneous state removing disruptions in the crystal lattice and improving corrosion resistance.

c. Age-Hardening. Another form of heat treatment which can alter the mechanical properties of certain alloys is age- or precipitation-hardening. Often the resultant metal state is less corrosion-resistant than the original. A discussion of this phenomenon can be found in any metallurgy text and will not be covered here.

d. Sensitization. Some stainless steels are subject to a phenomenon of heat treating known as sensitization. When heated in the range of 800 to 1600°F (425 to 870°C), they precipitate chromium carbide in the grain boundaries,

leaving the areas immediately adjacent to the boundaries low in chromium. Since 12 percent chromium is required for corrosion resistance in stainless steels, these areas are susceptible to corrosion. This problem has been observed frequently in welding of stainless steel. Resolution of this problem is attained by heating the steel to between 1800 and 1900°F (980 and 1040°C) whereupon the carbide redissolves. Quenching to room temperature completes the procedure, returning the steel to its former corrosion-resistant state.

3.3.6.4 Mechanical Deformation. During fabrication, metals are often plastically deformed. The term "plastic" here refers to permanent deformation, unlike elastic deformation such as is visible when a rubber band is stretched and released. Plastic deformation involves deforming and disrupting the metal grains; dislocations in the space lattice occur and high residual stresses are introduced. These areas are generally anodic to the remainder of the metal and, hence, will corrode more rapidly. Pitting, intergranular corrosion, and stress corrosion cracking may be encountered if annealing is not employed to reverse the effects of mechanical deformation.

3.4 THE ELECTROCHEMICAL SERIES. When two different metals or two like metals under different conditions are joined together electrically in a solution, they form a "galvanic couple". The corrosion of one of the metals (the anode) will be increased by the contact; the corrosion of the other metal (the cathode) will be decreased or stopped. In any practical situation, it is necessary to determine which metal is the anode and which, the cathode. This can be accomplished by comparing the corrosion potentials of the metals for the particular situation.

3.4.1 Corrosion Potentials and EMF. An electromotive force is defined as the force which tends to cause a movement of electricity through a conductor. In a galvanic couple, this force is the potential difference between the two electrodes.

3.4.1.1 Standard Potentials. The individual potential of a single metal can be measured relative to other metals. This potential will be different in different solutions. For convenience, a set of Standard Potentials has been devised, which indicate individual potentials relative to a specific set of arbitrarily assigned conditions. These potentials are measured relative to the "standard hydrogen electrode" which consists of hydrogen gas bubbled over a platinized platinum electrode immersed in a solution of unit activity (a definite hydrogen ion concentration). The metal

electrodes are immersed in one molal solution of their own ions. The potential of the standard hydrogen electrode is arbitrarily assigned the value of zero volts, and the other potentials are then measured from this standard.

A list of elements arranged according to their standard electrode potentials is defined as the electromotive force series, the sign being positive for elements with potentials that are cathodic to a standard hydrogen electrode and negative for elements with potentials anodic to a standard hydrogen electrode. The electromotive force series is shown in the Appendix. In most cases, any metal in this series will displace the more positive metal from a solution and thus corrode to protect the more positive metal. There are exceptions to this because of the effect of ion concentrations in a solution and because of different environments found in practice. This exception usually applies to metals close together in the series which may suffer reversals of potential. Metals far apart in the series will behave as expected, the more negative will corrode to the more positive. In an electrochemical reaction, the atoms of an element are changed to ions. If an atom loses one or more electrons (e^-), it becomes an ion that is positively charged and is called a cation (example, Fe^{++}). An atom that takes on one or more electrons also becomes an ion but it will be negatively charged and is called an anion (example, OH^-). The charges are shown in Appendix C. and coincide with the valence of the elements.

3.4.1.2 Reference Electrode. References other than the standard hydrogen electrode are sometimes used to determine electromotive series, because the hydrogen electrode is awkward to use in practice. Some common reference electrodes used in practical applications and their potentials relative to the standard hydrogen cell are given here:

<u>Half Cell</u>	<u>Potential (Volts)</u>
Tenth Normal Calomel	+0.3337
Saturated Copper Sulfate	+0.3150
Normal Calomel	+0.2800
Saturated Calomel	+0.2415
Silver-Silver Chloride	+0.2222
Hydrogen	0.0000

The electromotive series based on the standard hydrogen electrode is found in Appendix C.

A discussion of the copper-copper sulfate half-cell and other reference electrodes of interest in corrosion control work is found in Section 6.

3.4.1.3 Galvanic Series. The arrangement of a list of metals and alloys according to their relative potentials in a given environment is a galvanic series. By definition, a different series could be developed for each environment. Such a series has been developed for sea water. The series serves most practical purposes for metals used in the construction field. Galvanic series based on two different reference electrodes, calomel and copper-copper sulfate, are given in Appendix D.

The chromium-iron and chromium-nickel-iron alloys frequently change positions depending upon the corrosive media, particularly with respect to their oxidizing power and acidity, or to the presence of activating ions, such as halides. Inconel and occasionally nickel behave in a similar manner, though the variations in their positions are less frequent and less extensive. Although the relative positions of metals within a group sometimes change with external conditions, it is only rarely that changes occur from group to group. The metals within a group do not have a strong tendency to produce corrosion among each other and are relatively safe to use together. As the groups become more separated, the tendency for corrosion between the metals increases. The coupling of two metals widely separated in the list will result, therefore, in accelerated corrosion of the metal which is toward the anodic end of the series. For example, when steel and copper are coupled, the steel will corrode.

3.5 ELECTROCHEMICAL CELLS. Corrosion cells are of three basic types: the electrolytic cell, the galvanic cell, and the concentration cell. All are similar in that they have the four basic components, previously described: anode, cathode, electrolyte, and external metal conductor.

3.5.1 Electrolytic Cell. The electrolytic cell includes the four basic components plus an external source of electric energy connected in the external circuit between the anode and cathode to cause current to flow. This is the type of cell setup for electrically protecting structures by cathodic protection when electric power is available. It is also typical of the cell that exists when stray current corrosion occurs. (Figure 3-6a.)

3.5.2 Galvanic Cell. The galvanic cell, which has the four basic components, has an anode and cathode of dissimilar metals or dissimilar conditions of the same metal, in a

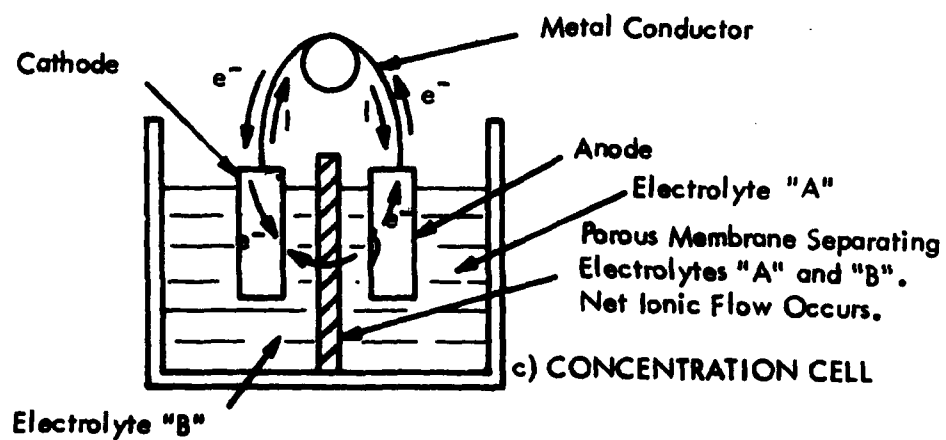
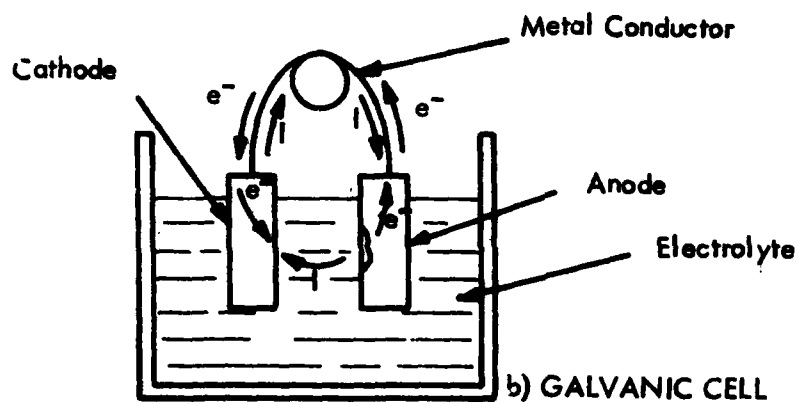
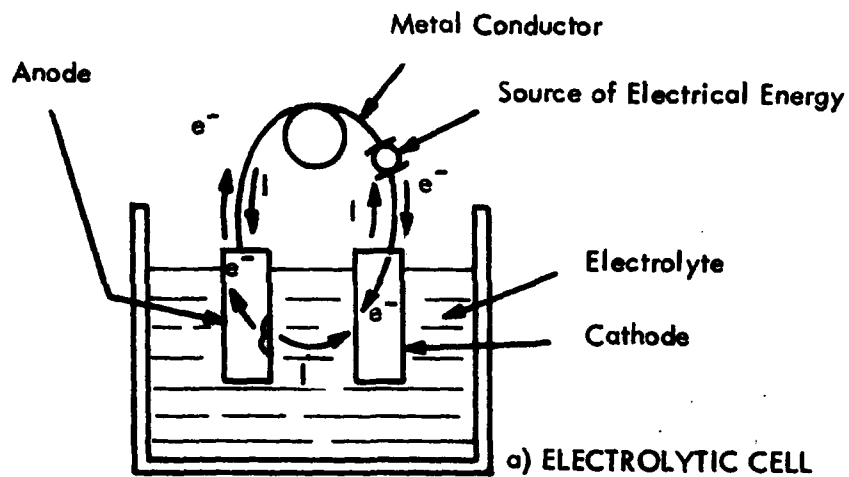


Figure 3-6
ELECTROCHEMICAL CELLS

homogeneous electrolyte. The common dry battery is a typical example. The dissimilarity causes one metal to become the anode and the other the cathode, thereby forming the battery action. Two different specified metals in the same electrolyte always produce the same potential (electrical pressure) between them. This type of cell is established when zinc, magnesium, or anodes of similar metals are used for protecting structures by cathodic protection when no direct current power is available. (Figure 3-6b)

3.5.3 Concentration Cell. The concentration cell is similar to the galvanic cell except with an anode and cathode of the same material in a nonhomogeneous electrolyte. The inequality of dissolved chemicals causes a potential difference which establishes the "anode" (usually the electrode in the more concentrated part of the solution). Differences of kind of chemicals will also produce potentials in a cell of this type. This type of cell accounts for most soil corrosion. These cells may be set up by variations in quantity of oxygen permeating the soil, by different concentrations of the same chemical, or by different kinds of chemicals. (Figure 3-6c) Conditions often occur also where electrochemical cells are a combination of the various types of cells.

3.6 CONVENTIONAL CURRENT AND ELECTRON FLOW.

3.6.1 Discussion. Conventional current flow was established at the time of Benjamin Franklin and was based on the "one-fluid" theory. By this theory, only positive electricity flowed, and the direction of flow was arbitrarily assumed to be from positive to negative.

This assumption was made before anything was known about the electron. This old conception of the direction of flow of the electric current is still retained and is called the conventional current flow. Electron flow is opposite in direction to conventional current flow.

It is emphasized that the electrons only flow in the metallic circuit portion of a corrosion cell. Current flow in the electrolyte (the direction of travel of the positive ions) is opposite in direction to the electron flow.

Figure 3-2 shows that positive ions are formed at the zinc anode and migrate toward the platinum cathode. In the electrochemical action that takes place on the surface of the zinc, which is in contact with the electrolyte, the zinc atoms give up two electrons (e^-) that will flow in the metallic circuit (external circuit) to the platinum cathode. These electrons reach the surface of the cathode and unite with two hydrogen (positive) ions forming a molecule.

It is emphasized that, in the electrolyte, the electric current flows from the anode to the cathode and is designated positive electricity. This designation of positive electricity is due to the positive charge on the ion which is the carrier of the current in the electrolyte. The direction of flow of the positive ions is the same as the conventional current.

On the other hand, the electron flow in the external circuit is from the anode to cathode and this is opposite to the direction of the conventional current. The electron flow in the external circuit is designated negative electricity because the electrons have a negative charge.

3.6.2 Polarity. In a galvanic or concentration cell, current flows according to the potential differences of the cell. The more anodic metal corrodes; the more cathodic metal is protected. Current flows from cathode to anode in the metal conductor (opposite to electron flow). Current flows from anode to cathode in the electrolyte (ionic flow).

In an electrolytic cell, current can be impressed either in the direction of natural current flow, or in the opposite direction. If the former case occurs, the anode and cathode remain the same as for the galvanic cell; however, a greater current sum of the natural and impressed currents is observed. In the latter case, if enough current is applied in the direction opposing the natural flow, the net flow will be the reverse of the galvanic flow. In this case, the metal which is anodic in the galvanic cell becomes cathodic, while the galvanic cell's cathode becomes the anode. The polarity of the cell has been reversed.

3.7 POLARIZATION. Polarization, by definition, is a change in potential of an electrode because of a current flow. This change is such as to decrease the potential difference between anode and cathode and, thus, reduce corrosion. As seen in Figure 3-7, for each of the three cases shown, the open circuit potentials of the electrodes (E_{ao} , E_{co}) at current I_0 change through polarization to some value (E_a , E_c) at lower current I_t . The potential difference decreases from the initial value of E_{t0} to E_t , the polarized potential.

3.7.1 Anodic, Cathodic, Mixed Control. Polarization of a corrosion cell is said to be "controlled" by whichever electrode polarizes. If both electrodes polarize appreciably, the reaction is said to exhibit mixed control (Figure 3-7a). If only one electrode polarizes, or one polarizes more rapidly, the reaction is under anodic (anode polarizes) or cathodic (cathode polarizes) control. (Figure 3-7b and c)

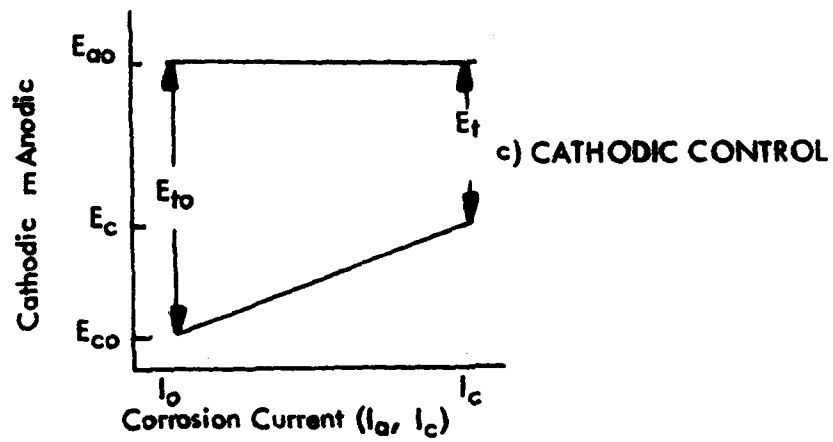
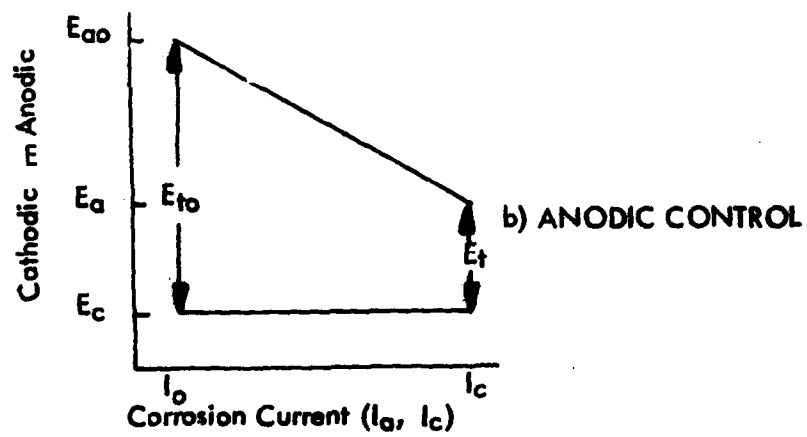
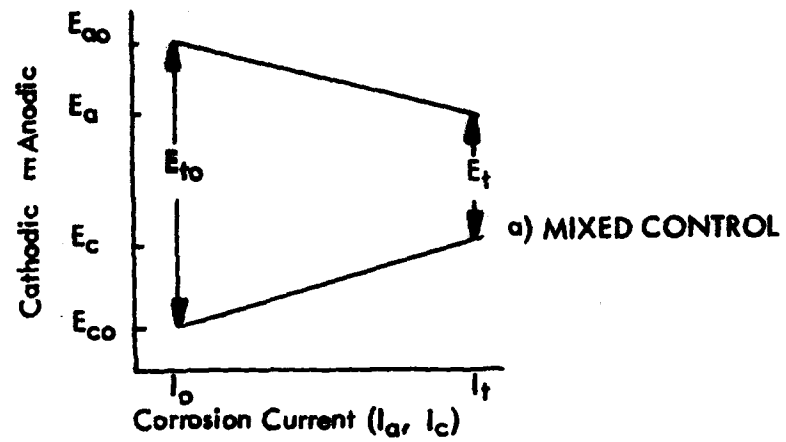


Figure 3-7
POLARIZATION

3.7.2 Mechanisms of Polarization. There are essentially three types of polarization, depending on the mechanism by which the corrosion reaction is slowed down. These are described here.

3.7.2.1 Activation Polarization. A corrosion reaction retarded by a slow step in the reaction sequence is said to exhibit activation polarization. A chemical or electrochemical reaction is actually a series of individual steps, any one of which may control the overall rate of reaction by being naturally slow to occur. When this situation arises at an electrode, the corrosion rate decreases. The formation of hydrogen gas from hydrogen atoms at the metal cathode is a slow step in the overall reaction of hydrogen ions to hydrogen gas. In strong acid solutions where this step is rate controlling, activation polarization is often observed.

3.7.2.2 Concentration Polarization. Concentration polarization results from concentration changes at the electrode-electrolyte interface introduced by the electrode reaction. Sometimes when a metal dissolves, the concentration of metal ions at the anode becomes so high that no more will go into solution. This is an example of concentration polarization. Another example, this due to low concentrations, is often observed in hydrogen evolution at the cathode in weak acid solutions. In a weak acid, the supply of hydrogen ions is low and may be rapidly consumed at the cathode. With no supply of ions, the reaction slows down, and the cathode becomes polarized.

3.7.2.3 IR Drop. Resistance polarization or IR Drop is perhaps the most common type of polarization. Here, corrosion is retarded by the build-up of reaction products, solids or films, on the electrode surface. Such a buildup results in an IR Drop which interferes with current flow and, consequently, slows the reaction. The hydrogen film commonly observed at the cathode surface is typical of the polarization mechanism. In this example, when current flows, deposition of a hydrogen film on the cathode surface tends to insulate the cathode from the electrolyte and builds up a resistance to the current flow. When this surface is completely covered with a hydrogen film which is of high electrical resistance, the current flow is substantially reduced and the cell is cathodically polarized. If corrosion is to continue, the hydrogen must be removed. If sufficient oxygen is present, the oxygen will combine with the hydrogen and thereby remove it. Oxygen is, therefore, a powerful depolarizing agent. The other way for the hydrogen to be removed is for it to bubble off as a gas.

This will happen only if there is sufficient energy supplied to overcome the tendency for the gas to adhere to the metal

(hydrogen overvoltage). If greater voltages than the hydrogen overvoltage are applied, gas will be liberated. Resistance polarization in dry batteries can practically stop current flow because the potential developed at the anode is not sufficient to overcome the high resistance of the hydrogen film. In this case, a depolarizer must be added to the electrolyte to remove the hydrogen so as not to impede corrosion because it is essential to the operation of a dry cell. Resistance polarization helps retard the natural corrosion of underground structures which are not cathodically protected, and helps reduce the current required to effect complete cathodic protection.

3.7.3 Cathodic Protection and Polarization. Cathodic protection is covered in Section 7. Mention of cathodic protection is made here to complete the discussion of polarization.

Cathodic protection is the impression of current on corroding metal surfaces. An external source, consisting of "artificial" anodes energized by rectified A.C. or galvanic voltage, is used. Where current leaves a metal surface, corrosion occurs. To stop corrosion, external current is applied in the opposite direction to that causing corrosion. This current makes surfaces exposed to the electrolyte become cathodic.

The criterion for determining adequate cathodic protection of these surfaces was originally proposed by Mears (reference 2) who states that complete "cathodic protection consists of polarizing the local cathodes up to the open circuit potential of the anodic area on the surface".

The open circuit potentials of the anode and cathode are identified in Figure 3-8 as E_{ao} and E_{co} . The open circuit potential difference, E_{to} , between the anode and cathode areas is determined by subtracting $E_{ao} - E_{co}$.

With the passage of time, and with no electrical, chemical or mechanical changes in the circuit, E_{ao} and E_{co} will approach the values E_a and E_c in Figure 3-8. Also, the corrosion current $I_a = I_c$ diminishes and stabilizes at a value corresponding to the stabilized potentials E_a and E_c . At some point, because of depolarizing agents such as O_2 , the current I_a reaches a steady state value as do E_a and E_c . This then represents the corroding structure.

In order to achieve complete cathodic protection, the local cathode must have a potential at least equal to E_{ao} . (dotted line, Figure 3-8) The current which accomplishes this also raises the anode potential to E_{ao} . Hence, $E_a = E_c = E_{ao}$ and no corrosion occurs. Any additional impressed current would continue to raise the anode and

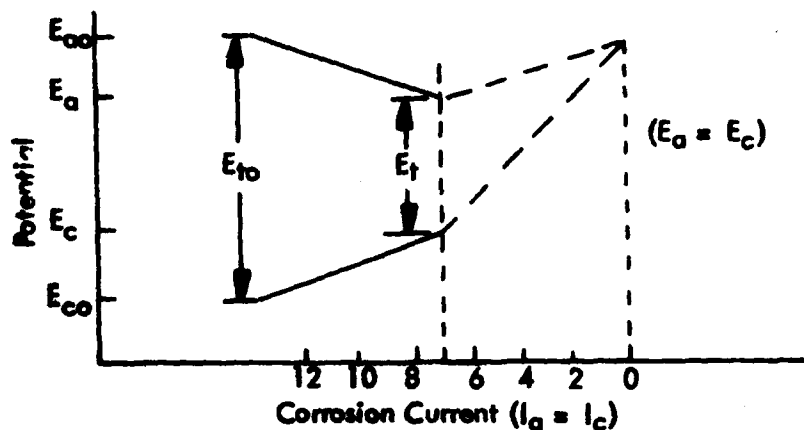


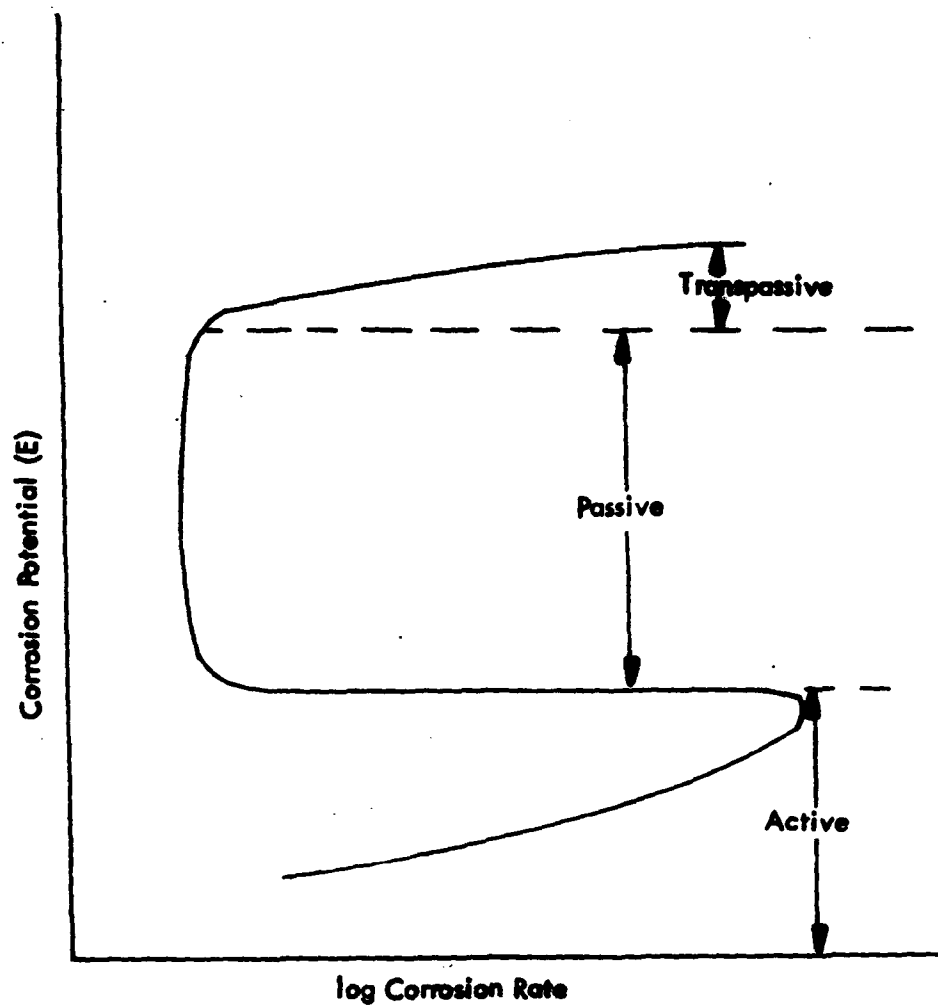
Figure 3-8
CORROSION CURRENT POLARIZATION EFFECT ON E_a AND E_c

cathode potentials, and supply a net current to the structure surface.

3.8 PASSIVITY.

3.8.1 General. Passivity is a phenomenon exhibited by metals (such as iron, nickel, or titanium) and alloys (stainless steels and others) under specific conditions whereby the anodic reaction rate of these metals is reduced. They become essentially chemically inert in environments where, according to the electromotive series, they should corrode.

A non-passivating metal exhibits increasing corrosion rate with increasing solution oxidizing power; a linear curve results on a semi-logarithmic graph. A passivating metal, however, exhibits the behavior of Figure 3-9. For low potentials, the expected linear increase is observed, as with a non-passivating metal; this is the area of the curve labeled "active". However, with a continued increase in the corrosion potential of the solution (oxidizing power), a sudden reduction in corrosion rate occurs. With further increased corrosion potential, no change in the rate is observed. The metal has become "passive". Often this passive corrosion rate is 10,000 times slower than the active rate. Then, at some higher oxidizing power, a return to a normal



log Corrosion Rate
Figure 3-9
CORROSION RATE OF A PASSIVATING METAL

linearly increasing rate is noted as the metal enters the "transpassive" region.

In the passive region these metals are truly corrosion resistant. However, for this resistance to occur, the oxidizing power of the metals' environment must remain in the definite range of passivity. Above or below this area, serious corrosion can occur.

The mechanism of passivity is not fully known. It is thought to be the result of a surface film formed under specific conditions which acts as a barrier between the metal and its surroundings.

3.8.2 Anodic Protection. Anodic protection of active-passive metals entails maintaining the passive region by application of an anodic current. A potentiostat is used to control the current and thereby maintain constant corrosion potential.

Very low currents are required to reduce the corrosion rate greatly in media that are normally very corrosive, and so this method of protection has found some applicability. Further discussion is found in paragraph 5.10.

SECTION 4 - EXAMPLES OF CORROSION

4.1 GENERAL. The definition of corrosion chosen by the National Association of Corrosion Engineers: "The deterioration of a material, usually a metal, because of a reaction with its environment" allows a very broad interpretation of what circumstances promote corrosion. Chemical, electrochemical, and physical changes may be so classified, depending on the materials and environments involved. For metals, circumstances are generally electrochemical, but this does not mean that metals corrode in only one way. In reality, corrosion of metal most often involves a variety of conditions, many of which alone could result in deterioration. Examining a real corrosion problem may entail recognition of several sources of corrosive action.

4.2 GALVANIC CORROSION. Galvanic corrosion results from a galvanic cell. Galvanic cells consist of anodes and cathodes of different metals or the same metal under different conditions in a homogeneous environment. (paragraph 3.5.2.) These electrodes are connected together metallurgically and by an electrolyte, completing a basic corrosion cell.

The galvanic cell can take on many forms, the most important of which are discussed here.

4.2.1 Dissimilar Metals. When two dissimilar metals are metallurgically coupled and placed in an electrolyte, current flows (in the electrolyte) from one to the other. The metal from which current is flowing (the anode) will corrode, and the metal to which current is flowing (the cathode) will be protected from corrosion. This type of corrosion is termed galvanic and is sometimes referred to as bimetallic corrosion.

Examples of galvanic corrosion are shown in Figures 4-1 and 4-2. In Figure 4-1, the two dissimilar metals are copper and steel. The space between them is filled with an electrolyte, or current-conducting medium. The external circuit is completed through the metallic junction of steel and copper, which permits a current to flow from the steel through the electrolyte to the copper. Where current leaves the steel, it carries charged particles of iron, or ferrous ions (Fe^{++}), into the electrolyte. Steel corrodes or loses weight as charged particles go into solution. If the external circuit is opened or a sufficiently high resistance is introduced into the circuit, electric current flow is stopped or reduced and corrosion is altered accordingly.

In dissimilar metal couplings, the more active metals in the galvanic series corrode to protect the more noble metals. (paragraph 3.4.) The galvanic series (Appendix D)

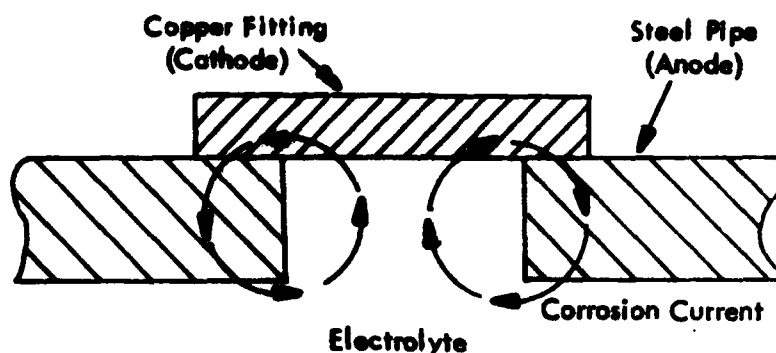


Figure 4-1
GALVANIC CORROSION: DISSIMILAR METALS

shows the relative tendency of metals to corrode when coupled in a given electrolyte.

4.2.2 Various Conditions in the Same Metal. Galvanic corrosion is not limited to metals easily recognized as being dissimilar, such as steel and copper. Substantial galvanic potentials can exist between surfaces normally considered to be of the same metal. Examples of such galvanic cells are:

- (1) Steel is anodic to the mill scale found on hot rolled steel products, such as pipe and steel piling.
- (2) New steel is anodic to old steel.
- (3) Brightly cut surfaces, such as pipe threads, are anodic to plain surfaces.
- (4) The more highly stressed surfaces, such as pipe bends, are anodic to normal surfaces.
- (5) Surface imperfections and nonhomogeneities of metals cause galvanic cells to exist.

Galvanic cells resulting from dissimilar conditions may be of minor importance. Generally, however, the results are important and cannot be ignored. Often a section of new pipe inserted in an old pipeline will fail from corrosion within a few years. Maintenance personnel often conclude that the new pipe is not as well made as the old pipe. Similarly, the corrosion failure at pipe threads is often blamed on the thinner metal section at the threads, whereas the actual cause is a galvanic cell, a small area of bright metal coupled with a large area of metal in a less active state. Figures 4-3, 4-4 and 4-5 illustrate typical galvanic cells. They do not show all types of galvanic corrosion, but are a guide against improper use of dissimilar metal



Figure 4-2

GALVANIC CORROSION OF STEEL
PIPE CONNECTED TO BRONZE VALVE

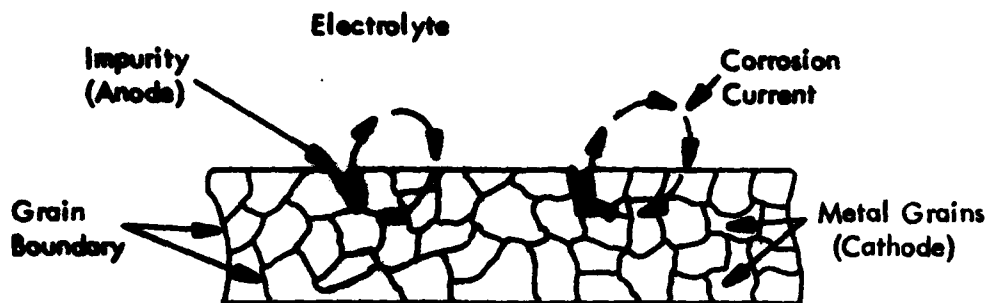


Figure 4-3
GALVANIC CORROSION DUE TO IMPURITIES IN THE METAL

couplings.

4.3 ENVIRONMENTAL DIFFERENCES.

4.3.1 General. When metal is placed in contact with an electrolyte which changes composition as new constituents are produced by reaction, corrosion usually occurs. When metal is placed in contact with an electrolyte having different constituents from point to point or different concentrations of constituents from point to point, corrosion may also occur. This is differential environmental corrosion. Corrosion results from a difference in composition of the electrolyte in the first two cases and from the difference in concentration in the third case. All three cause corrosion of metals.

A metal's potential is unique to the individual environment in which it is measured. In theory, no corrosion cells will occur in a homogeneous or uniform environment. This is rarely found in practice. As a result, potential gradients exist between the portion of metal in one environment and the portion in another. Sometimes these conditions produce serious corrosion.

Many opportunities exist for differential environmental cells on underground metal structures, such as:

- (1) Nonuniform texture or type of soil in contact with a structure
- (2) Nonuniform moisture conditions in the soils in contact with a structure
- (3) Differential aeration in the soils in contact with a structure
- (4) Presence of foreign matter in the soils in contact with the structure, such as metallic objects



Figure 4-4

CORROSION OF PIPE THREADS, ANODIC TO
SURROUNDING METAL (HOT WATER LINE)

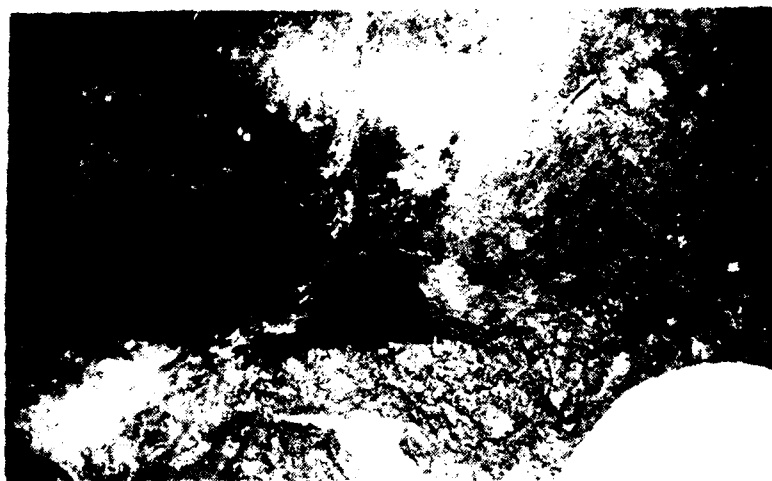


Figure 4-5
PREFERENTIAL CORROSION OF
WELD ON COOLING WATER LINE

(5) Bacterial action in the soils (paragraph 4.4).

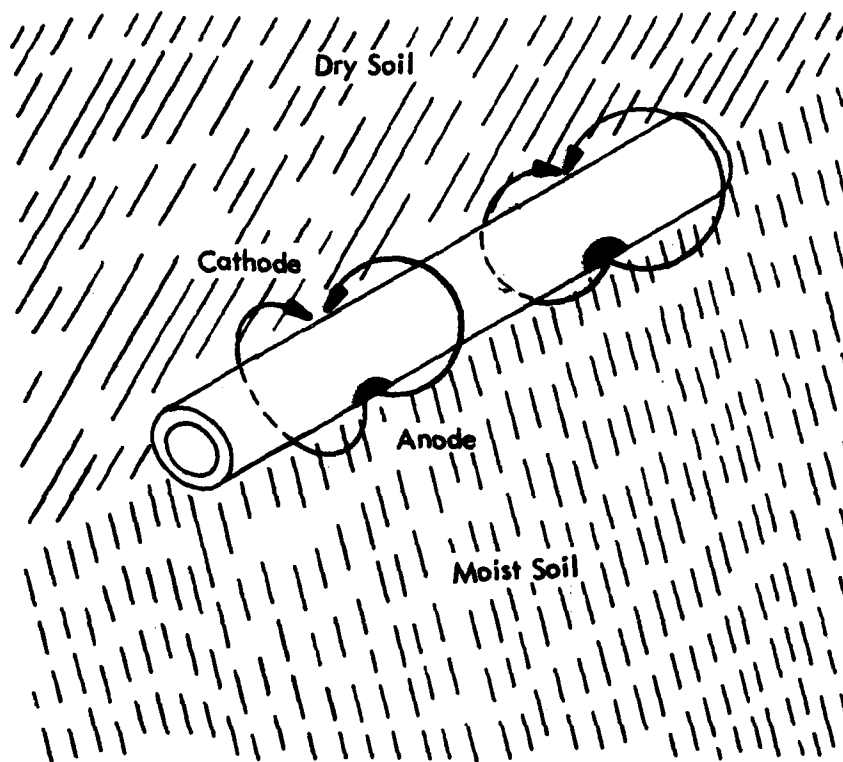
Corrosion cells resulting from differential environmental conditions may be very large or very small. (Figures 4-6 and 4-7.) Examples of small cells are a lump of clay in contact with a pipe otherwise surrounded by a sand loam, and pipe lying within a trench that is wetter on the bottom than on the top. Large cells, such as those producing long-line current, may occur where a pipeline runs through a moist area into a dry area or from a low soil resistivity area into a high soil resistivity area.

One differential environment cell commonly encountered with underground pipes is the soil-concrete cell. Where pipe enters a building wall underground, part is in soil and part is in concrete. Failures are often found in the soil-enclosed pipe immediately adjacent to the wall, where proper insulation, such as a dielectric wall sleeve, has not been employed.

Long steel structures, such as load-bearing piles and sheet piling driven into the earth, are especially susceptible to corrosion from differential environmental conditions. When piles terminate in large concrete caps, are interconnected to copper grounding systems, or are exposed to a severely corrosive environment or stray currents, they may corrode rapidly. Often, when driven into undisturbed soil and not encumbered with massive concrete caps or copper grounding, etc., they are no problem.

Romanoff, of the National Bureau of Standards, showed after extensive testing of isolated piles and elements of a large expanse of bulkhead (reference 3) that no appreciable corrosion occurs in undisturbed soil, but corrosion does occur more extensively in the water table and fill areas. Sudrabin agrees that low corrosion rates exist in undisturbed soil, and points out that severe corrosion has been found on upper portions of piles (reference 4). DeMarco has reported severe corrosion of H piles in rubble fills of 2500 ohm-cm resistivity (reference 5).

Water stratification between salt and fresh water in harbors and rivers may also produce an environmental change. Figure 4-8 shows differential environmental corrosive action resulting from stratification of sea water and fresh water. This type of corrosion frequently occurs in rivers, harbors, and estuaries where stratification of water occurs all or part of the time.



Cathode Area

Anode Area

Cathode Area

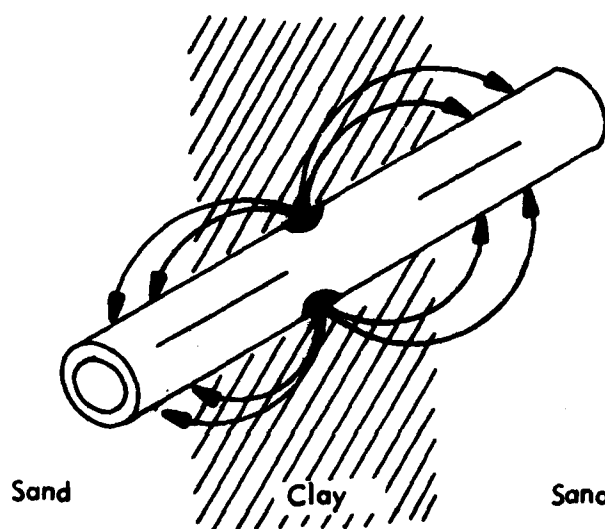


Figure 4-6
SMALL CORROSION CELL DUE TO DISSIMILAR SOIL CONDITIONS

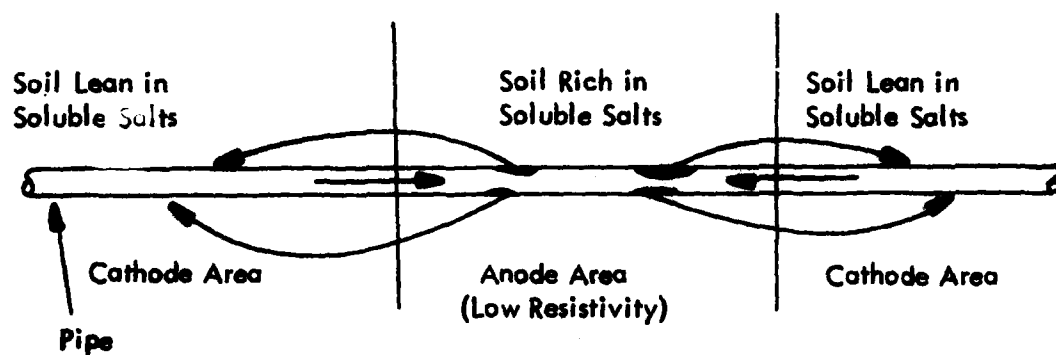
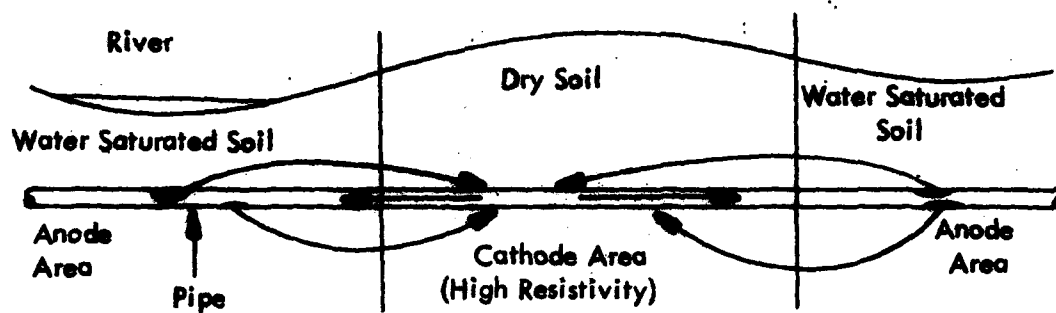


Figure 4-7

LONG LINE CURRENTS: DIFFERENTIAL ENVIRONMENT

Local differential environment cells may occur in corners and at welds on marine or other structures. Differential environmental corrosion of this type can cause a great deal of damage in sheet pile construction. If holes are cut in the sheet piling for the attachment of tie rods, water action often causes a small pocket to be hollowed out immediately behind the sheet piling. If the pocket is filled with water or a lower resistivity electrolyte than the surrounding earth, a local corrosion cell with a small anode area and a large cathode area exists. The result may be corrosion of the tie rods, and this proceeds until the section is so reduced that the tie rod suffers a tensile failure. This condition is shown in Figure 4-9.

4.3.2 Concentration Cells. Environments consisting of different materials are not the only ones which produce corrosion. Concentration variations also induce potential gradients on metals, resulting in concentration cells. Two common types of concentration cells contribute to local corrosion. These are ion concentration cells or oxygen concentration (differential aeration) cells. The former refer to different concentrations of

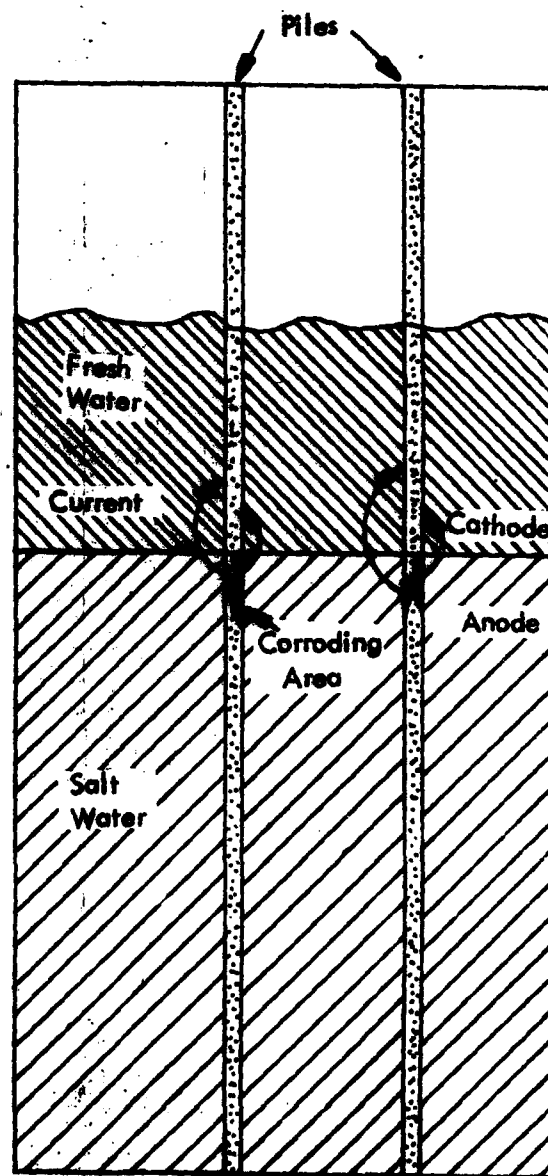


Figure 4-8
DIFFERENTIAL ENVIRONMENT CELL
CAUSED BY WATER STRATIFICATION

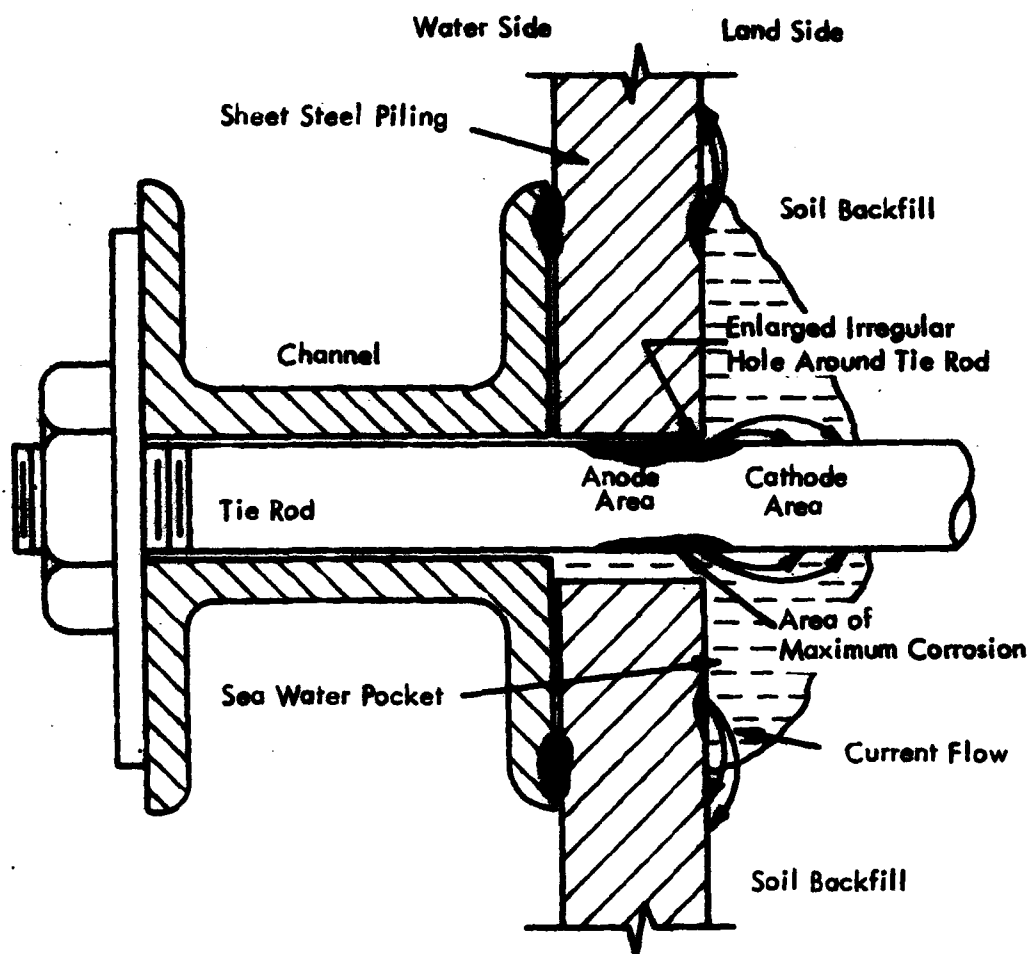
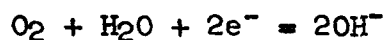


Figure 4-9
CORROSION AT TIE ROD

metallic ions in various parts of a solution, whereas the latter refer to variations in oxygen content at different areas in contact with metal. Where a large object, such as a pipeline, passes through different soil environments, major corrosion cells extending over several miles may be established resulting in long-line currents on the structure. Several amperes of current may flow in the metal of a pipeline as a result of such conditions. Corrosion occurs where current leaves the pipe surface.

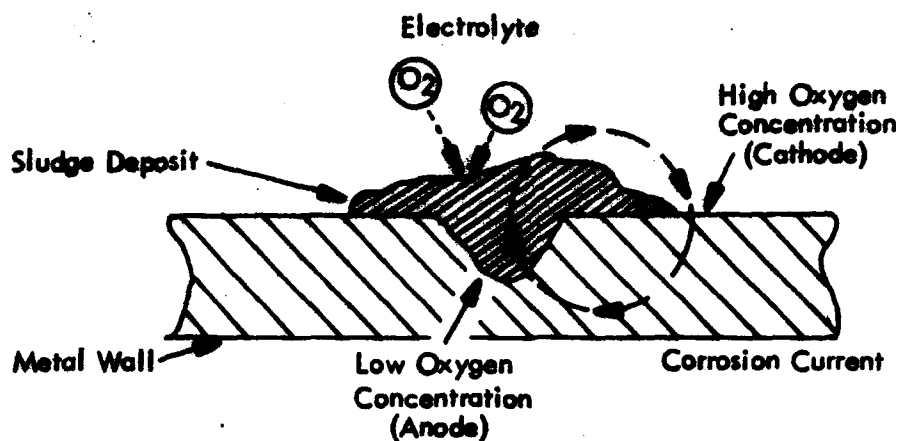
Pipelines or underground tanks placed in trenches and back-filled are subject to oxygen concentration cells. (Figure 4-10.) Oxygen is used up at areas of high concentration according to the oxidation reaction:



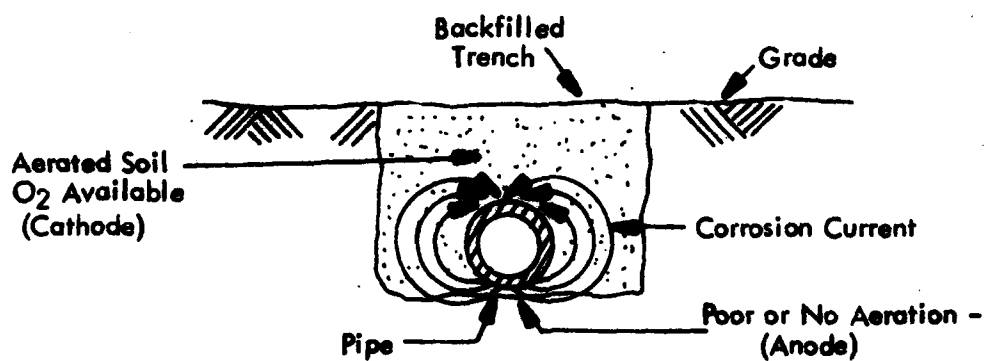
Since oxidation occurs at cathodes, areas of high oxygen concentration become cathodic to areas of low oxygen concentration. Less oxygen is found at bottom surfaces of tanks or pipes, so accelerated corrosion occurs there.

Small corrosion cells may result from differential aeration on pumps or sludge digesters under rust tubercles (Figure 4-11). Similar problems occur in steam condensate lines and hot water lines, resulting in damage to the structures as shown on Figures 4-12 and 4-13. Differential cells also occur in connection with certain forms of marine growth and sometimes at a water-soil interface as the result of scouring action. Harbor contamination may result in differential environments, either in the water or between the water and silt on the bottom. Contamination may also promote bacterial action, thereby intensifying differential environmental conditions resulting in increased corrosion attack, even in very deep water.

Corrosion on sheet piling in sea water, where the water level changes due to tide or wave action, is often due to differential aeration cells. Figure 4-14, a corrosion profile for sheet piling in sea water, shows two major zones of attack, one at the high-tide elevation and another below the low-tide elevation. The first zone is due primarily to atmospheric corrosion. The second zone of attack occurs because of differential aeration. The corrosion cell is formed by the cathodic (aerated) area between low and high tides and the anodic (unaerated) area in the continuously submerged zone. The corrosion profile illustrated in Figure 4-14 is for a specific piling. The profile may differ greatly, depending upon conditions at a given location. Sometimes additional corrosion cells are concentrated just below low-tide elevation and in the earth region. In the first case, corrosion occurs when surface water is highly aerated and the differential aeration cell here is



a) DIFFERENTIAL AERATION UNDER SLUDGE DEPOSIT



b) DIFFERENTIAL AERATION IN TRENCH

Figure 4-10
OXYGEN CONCENTRATION CELLS

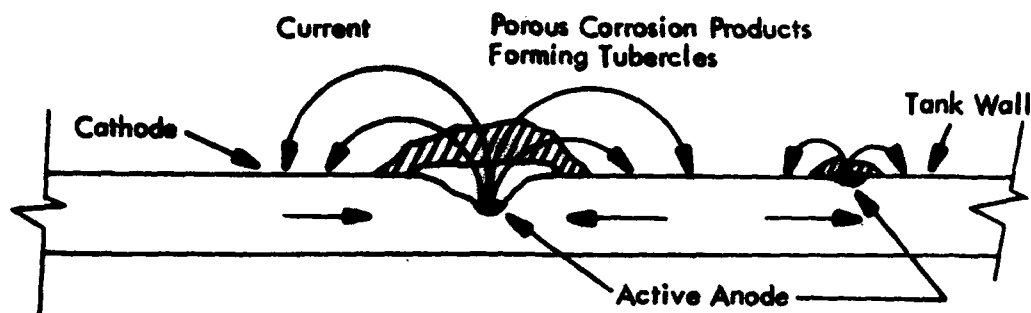


Figure 4-11
RUST TUBERCLE ON TANK WALL

accentuated. Examples of corrosion just below low-tide elevation are found on piling in areas subject to moderate wave action.

4.3.3 Crevice Corrosion. Crevice corrosion is another problem resulting from differential environment conditions. Due to reaction, the chemical composition of a solution in a crevice changes. Corrosion results. Crevice corrosion can be mitigated by either enlarging the crevice to allow the solution therein to remain in balance with the mass of solution, or by filling in the crevice with some non-corrosive. This type of corrosion may be found in crevices built into a structure, or where some object has been placed or dropped on a surface and a small film of solution exists beneath it.

4.3.4 "Cathodic Corrosion". Another source of corrosion caused by environmental change is cathodic reaction products. Corrosion from cathodic products is often termed "cathodic corrosion". In lead-sheathed cables, a potential exceeding -1.20 volt to a copper-copper sulfate reference electrode, particularly in a highly alkaline environment, will cause alkaline products to form at the cathode. These alkaline products are corrosive to lead. This same effect occurs whether lead cables are purposely placed under cathodic protection or bonded into a cathodic protection system and the cable held in excess of -1.20 volt. Aluminum also will be corroded under similar conditions and should be maintained at a potential of less than -1.20 volts to a copper-copper sulfate half-cell. Consequently, correction of stray current conditions by bonding and cathodic protection systems must be carefully adjusted where lead and aluminum are involved. In addition, these metals should not be placed in alkaline environments, where similar problems will arise such as aluminum in concrete.



Figure 4-12

RUST TUBERCLES INSIDE STEAM CONDENSATE LINE

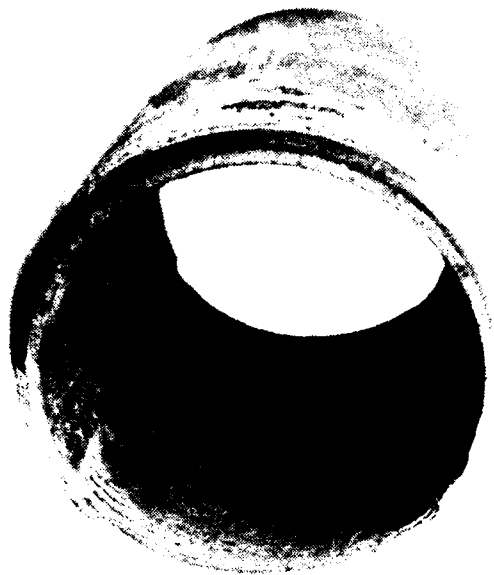


Figure 4-13

CARBON DIOXIDE CHANNELING
STEAM CONDENSATE LINE

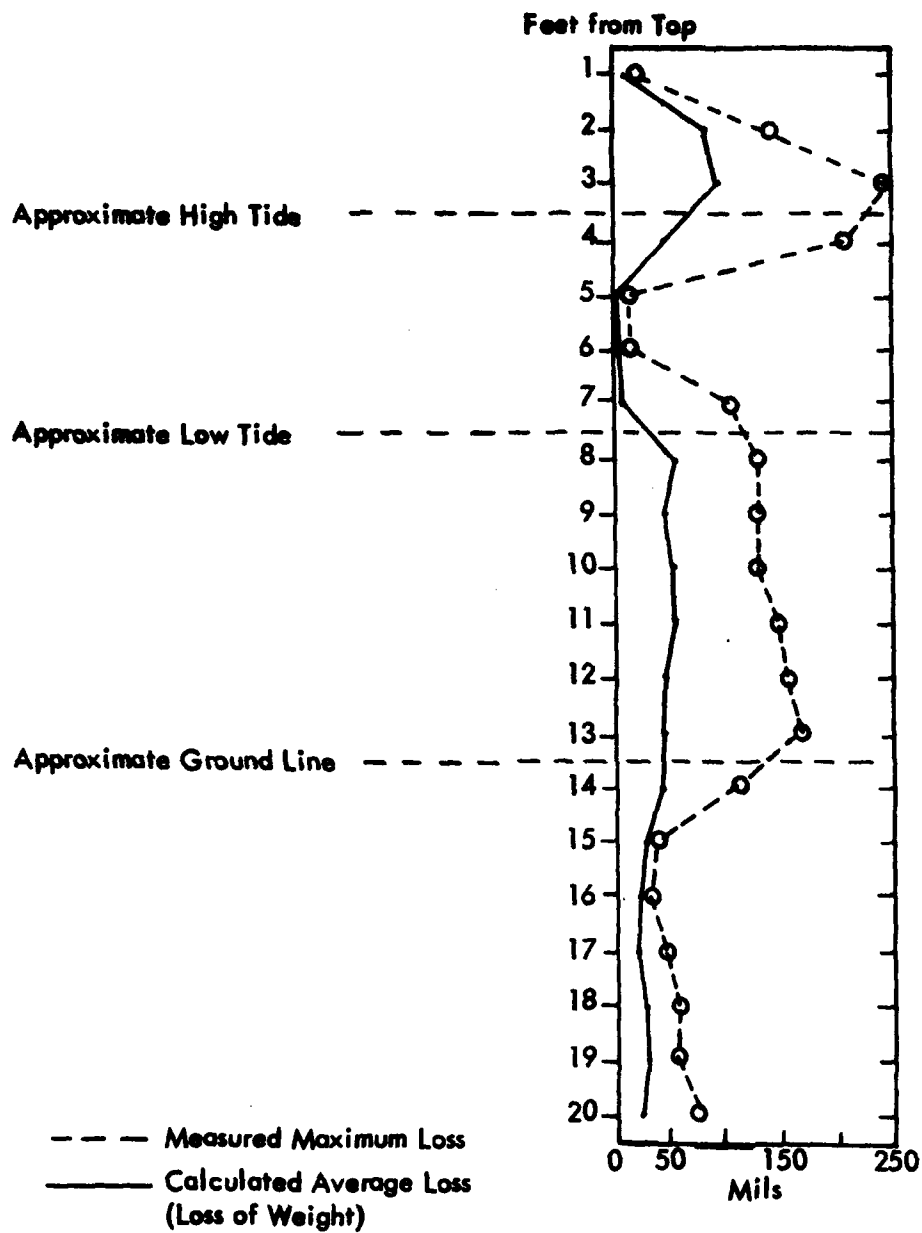


Figure 4-14
CORROSION PROFILE OF SHEET-PIILING IN SEA WATER AFTER FIVE YEARS

This corrosion can be controlled as long as the protective current is held constant. If protective current is reduced or interrupted, alkaline products attack the metal (lead and aluminum). It is advisable to keep cathodic protection current continuous to avoid corrosion by cathodic products.

Examples of differential environmental cells are shown in Figures 4-15 through 4-18. Note that variations in moisture content, availability of oxygen, change in soil resistivity, or variations of all three sometimes occur. As in all corrosion phenomena, environmental changes or variations are a contributing factor.

4.4 BACTERIOLOGICAL CORROSION. It has been known for several years that one phase of corrosion is due to anaerobic soil bacteria. Corrosion takes place as a result of sulfate-reducing bacteria. This is not found in all soils. Some pipe coatings are thought to serve as food for bacteria.

The mechanisms by which microbiological corrosion takes place are obscure in many cases. The general effect, however, is to create a change or difference in local conditions. Organisms can contribute to corrosion by any or all of the following:

- Creating differential electrolyte concentration cells on the metal surface

- Creating a corrosive environment as a result of their life cycle and products of decomposition

- Acting as either anodic or cathodic depolarizers.

4.4.1 Forms of Microorganisms. In almost any soil or water, there are many varieties of microorganisms. Both aerobic (oxygen using) and anaerobic (nonoxygen using) can exist in a given environment in varying quantities, depending on conditions of nutrition, temperature, moisture, season, and similar factors. Aerobic bacteria will naturally occur in quantity where oxygen is readily available; anaerobic bacteria occur most plentifully where oxygen is not readily available. Both varieties, however, may exist side by side in a given environment, and members of both groups can cause corrosive conditions. The anaerobic sulfate-reducing bacteria, *Sporovibris desulfuricans*, are generally believed to be the most responsible for corrosion of ferrous materials. Such bacteria are exceedingly prevalent and cause extensive damage. The mechanisms by which bacteria promote corrosion have been studied both in the field and in the laboratory. A number of reactions that take place under environmental conditions favorable to anaerobic bacterial corrosion have been defined as a result of such investigative work.

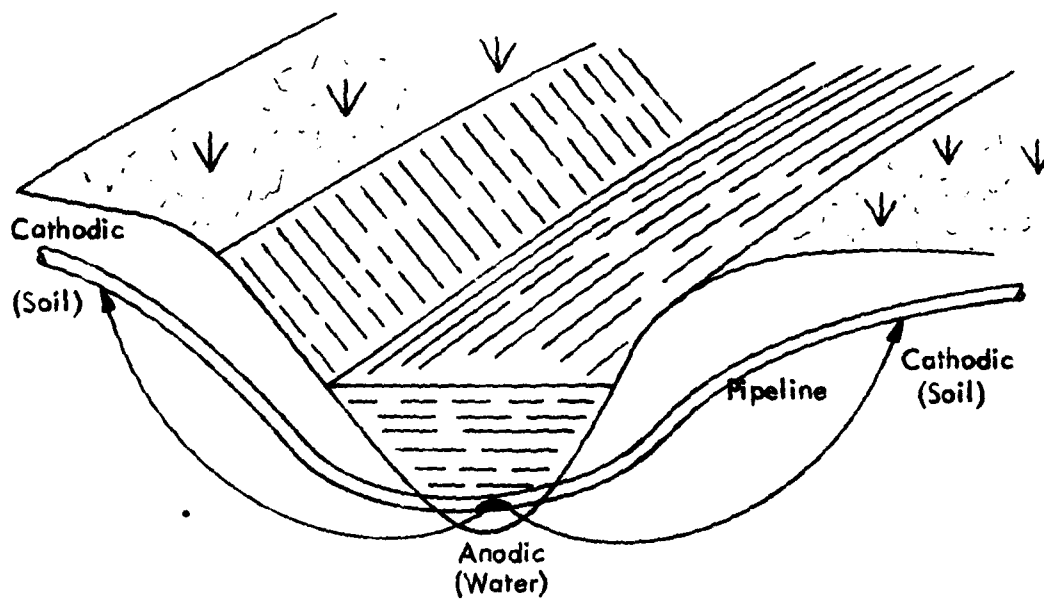
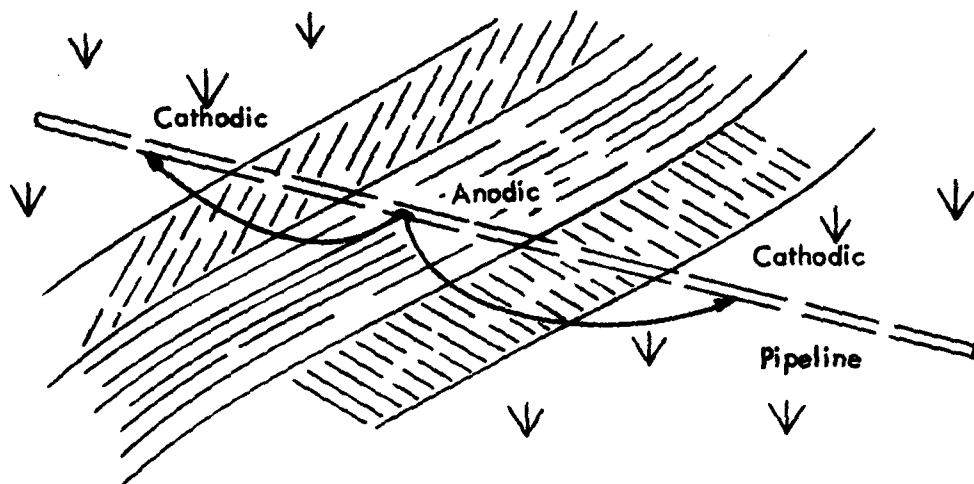


Figure 4-15
CORROSION CAUSED BY DISSIMILAR ENVIRONMENTS



Figure 4-16
SOIL CONCRETE CELL
RADIANT HEAT PIPE



Figure 4-17

SOIL CONCRETE CELL - PIPE BOTTOM IN
SOIL ANODIC TO REMAINDER IN CONCRETE



Figure 4-18
OXYGEN CONCENTRATION CELL
INSIDE BRASS WATER LINE

4.4.2 Favorable Environments. Corrosion caused by anaerobic bacteria occurs in soil and both fresh and salt water. The necessary conditions are the lack of oxygen and the presence of sulfates. Such states occur in bogs; water-logged soils, such as heavy clays and swamps; contaminated waters; and stagnant low-oxygen-content fresh waters. Water containing waste from paper-making operations is especially rich in sulfate-reducing bacteria. Anaerobic bacteria are a chronic source of trouble in paper manufacturing. Because corrosion usually takes place in the presence of oxygen, it is important to realize that corrosion caused by anaerobic bacteria takes place where there is a deficiency of oxygen. Corrosion can occur both on the inside and on the outside of piping and tanks where there is a deficiency of oxygen.

Piping and tanks containing water that is deficient in oxygen may suffer from corrosion caused by anaerobic bacteria. A common example is a water tower that is used for stand-by fire-fighting purposes. Because the water must be available at all times, it is allowed to become stagnant. Bacterial growth, accompanied by oxygen deficiencies in the water, may result in corrosion.

4.4.3 Corrosion Products. Corrosion products associated with anaerobic bacterial corrosion are black and consist of compounds which include ferrous sulfide in the case of iron or steel. They are easily recognized when examined immediately after excavation - a gray "frost" covers the black "paste". When the paste is washed from steel with water, shiny bright metal appears under it. Corrosion attack is a "slabbing" (tree bark appearance), rather than pitting.

4.5 SELECTIVE DISSOLUTION. "Selective dissolution" refers to the removal, by corrosion, of one of the materials that make up an alloy. Dissolved material is always anodic to the remainder.

Selective dissolution is characterized by increased brittleness, extreme lowering of tensile strength, porosity, and in many cases a color change. At times, no visible loss of metal is evident such as cracks or pits in the metal surface. Often the surface roughens somewhat. Sometimes referred to as selective leaching or dealloying, this type of corrosion also is named according to the alloy involved. "De-zincification" of brass (removal of zinc) and "graphitization" of cast iron (removal of iron, leaving graphite) are among the most commonly observed examples of selective dissolution.

Dezincification of brass occurs in water which is high in carbon dioxide content, i.e. soft water. Here corrosion is increased by chlorides in the water, stagnation and high water temperature. Dezincification appears as a color change, distinctly reddish. Often, "plug type"

dezincification occurs. A localized area is attacked, leaving a plug of porous copper in the metal wall.

Cast and ductile iron often exhibit selective dissolution known as graphitization in salt water, acid soil and solutions, or in areas high in sulfate content.

Cast and ductile iron differ from steel in that they consist of flakes or nodules of graphite (carbon) in an iron matrix. Corrosion of these metals causes a loss of the ferritic constituent, thus leaving the graphite and products of corrosion. This phenomenon, graphitization, affects cast and ductile iron about the same. Graphitized pipe often retains the appearance of sound pipe, leading observers to believe that the structure has remained corrosion free for many years. However, it responds with a dull sound when struck with a metal object and can easily be "dug into" with a screw driver. It lacks the strength of the original iron. If not subjected to external or internal stress, graphitized pipe will often give long, leak-free service.

Three types of graphitization are surface, plug, and complete. Surface-type graphitization results in the formation of a graphite film on the pipe. Corrosion then virtually ceases and iron beneath the film remains intact. This is expected in uniform, high resistivity soils. Romanoff (reference 6) has shown that, in well-drained soils of resistivity above 5,000 ohm-cm, corrosion of cast iron proceeds at a rapid rate for 3-5 years and then slows to an insignificant rate. Surface-type graphitization may well account for this phenomenon.

Plug-type graphitization leads to the development of plugs of graphite in the pipe wall. Plugs occur at anodic pipe areas, often caused by heterogeneous backfills. For example: clods of clay may become mixed with sand. Failures occur when plugs blow out from increased water pressure, water hammer, or when an external stress causes the pipe to break at areas weakened by them. A failure is usually characterized by a large hole in the pipe wall. (Figure 4-19.)

The ultimate in cast-iron corrosion is complete graphitization. Here, all the iron constituents have been lost and only a graphite shell remains. Such pipe may give leak-free service provided it is not subjected to stresses. Stresses are often created, however, by heavy vehicles, nonflexible pipe joints, soil conditions, water hammer, and beam action. As the graphite shell retains little strength, it cracks, often circumferentially. As pipe appears sound, such failures are not often recognized as corrosion but are usually referred to merely as "main breaks".



Figure 4-19
"BLOW-OUTS" OF GRAPHITIZED CAST IRON LINE

4.6 **EXFOLIATION.** Exfoliation is a phenomenon in which entire layers of the metal are corroded away, beneath the surface. Resulting corrosion products are expansive and force the grains apart, giving the corroded metal a laminated appearance. Blistering and lamellar separation are often observed. In extreme cases the edge of a corroded sample may resemble a warped and broken deck of playing cards.

Generally instigated by cold work, exfoliation has been successfully prevented by heat treatment and alloying. Aluminum and aluminum alloys are most often associated with this deterioration.

4.7 **CAVITATION.** Cavitation is a form of erosion corrosion which occurs when liquid in contact with a metal surface is subjected to rapidly changing pressure. Water under high velocity causes turbulence. This turbulence reduces pressure on the liquid in local areas. When pressure is reduced rapidly at a local area, boiling occurs, forming small cavities of vapor. The return of pressure to normal causes an implosion as cavities collapse, resulting in high-speed liquid impact on the metal surface. The metal surface work-hardens, roughens, and cracks by fatigue, causing a deep, spongy pitting.

In metals normally protected from corrosion by a surface film, the implosion breaks the film resulting in damage to the metal surface. Cavitation in domestic copper hot water lines is frequently observed. The use of more resistant alloys or design criteria which minimize areas of turbulence will improve metal performance.

Cathodic protection has also proved successful to reduce cavitation damage for many materials and corrosives. In particular, galvanic anodes have been attached to ship hulls in the region of expected damage from propellers. These successfully prevent hull deterioration from cavitation. Cavitation of a pump impeller after operation in sea water is shown in Figure 4-20.

4.8 **IMPINGEMENT.** Cavitation is often accompanied by another form of erosion corrosion - impingement. Fast-moving liquids with entrained solids or gases often result in this form of corrosion. Abrasion due to rapidly moving liquid and entrained particles wears away the metal's protective surface film. Repetitive destruction of this film gives rise to a pattern of localized, smooth-bottomed pits. These pits are characterized by undercutting metal in the direction of flow and a lack of corrosion products (Figure 4-21). It is generally thought that impingement damage is not appreciable below a threshold velocity characteristic of the metal, the temperature, and the specific fluid in

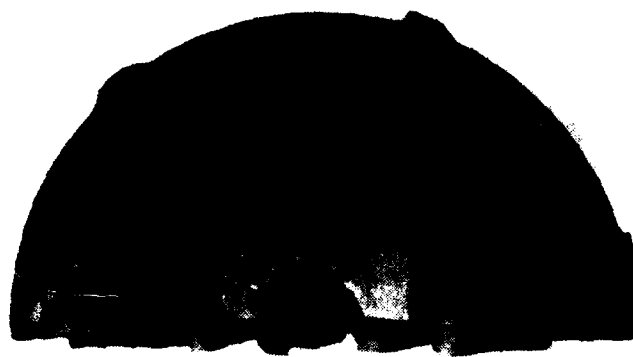


Figure 4-20
CAVITATION CORROSION OF PUMP IMPELLER



Figure 4-21

IMPINGEMENT OF COPPER WATERLINES

question.

4.9 FRETTING CORROSION. The mechanism of fretting corrosion, which occurs on closely fitted metal parts under load and vibration, is not well known. A common example is a ball-bearing race pressed on a shaft. When fretting corrosion takes place, the contacting surfaces become pitted in areas. Even forced and shrunk fits are subject to this type of corrosion. The damage to steel is evident from a deposit, usually red in color, that forms at the interface, resulting from the pitting of the metal. Such damage creates uncertainty in the operation of machinery because it destroys close tolerance and increases the possibility of failure.

Two theories have been advanced to explain the rate of corrosion in fretting. The first theory suggests that heat from friction between the rubbing surfaces results in welding and subsequent fracture and crumbling of adjacent surfaces. These particles corrode in the existing environment, and the process continues on the roughened surface.

The second theory proposes that relative motion of the surfaces wears away the protective film, resulting in corrosion.

Fretting is observed in almost all alloys, under the proper conditions. This form of corrosion can be prevented by several means. Lubrication between the surfaces can eliminate the problem. Roughening the surfaces or increasing the load to prevent slip will often help, as will greatly increasing the relative movement at the interface. The use of harder materials may also mitigate fretting corrosion.

4.10 STRESS CORROSION CRACKING. Stress corrosion cracking is the result of tensile stress, applied or residual, combined with a corrosion environment. It is a common cause of failure in many alloys, and was initially observed as "season cracking" of brass cartridge casings and "caustic embrittlement" of riveted steam boilers. Stainless steel is especially susceptible, and even exotic metals often fall prey to stress corrosion under specific conditions.

It is generally thought that the tensile strength needed to produce stress corrosion must be above the metal's yield strength, although conditions vary somewhat depending on the environment. The stress can be residual stress, as caused by cold-working or cold-forming, or it may result from welding or applied loads. Tensile-stress components are required for cracking.

Only mildly corrosive environments are necessary to produce stress corrosion. Without the stress, these environments

might normally not cause much corrosion damage. It is the combination of tensile stress and corrosive environment which results in failure by cracking.

Stress corrosion cracks may be either intergranular or transgranular. (Figures 4-22 and 4-23.) In either case, there is little actual weight loss; failure occurs by cracking.

Austenitic stainless steels are especially subject to this type of corrosion, usually in environments containing chlorides. The chlorides concentrate in crevices in the structure and result in costly failures. By lowering chloride content of the environment or by eliminating crevices in the system design, some relief from stress corrosion cracking in these materials has been achieved.

Another form of stress cracking is caused by hydrogen. Hydrogen in the atomic state can permeate the lattice of many metals, resulting in loss of ductility (hydrogen embrittlement). If sufficiently high tensile stress is also present, failure by hydrogen cracking may occur. This type failure is similar in appearance to stress corrosion cracking. It is generally transgranular, but may follow an intergranular path. Atomic hydrogen can be produced on a metal surface by a corrosion reaction, or by cathodic protection. Some of the hydrogen atoms combine to form molecular hydrogen and evolve as a gas. Other atoms are absorbed into the metal where they congregate at voids or other lattice defects. The pressure resulting from this can cause cracking in stressed conditions or blistering of the metal surface. Prevention of hydrogen embrittlement and cracking is accomplished by eliminating the source of hydrogen or choosing less susceptible materials. This condition is common in steels.

4.11 CORROSION FATIGUE. Fatigue failure of a metal due to repeated cyclic stresses below the tensile strength is observed in non-corrosive environments. The presence of a corrosive environment greatly decreases, often by as much as one-half, the stress required for failure. The accelerated cracking failure is "corrosion fatigue", related to stress corrosion cracking. (Figure 4-24.)

4.12 HIGH TEMPERATURE CORROSION. Oxidation is the most common high temperature corrosion reaction. Oxidation, like most reactions, increases in rate with temperature, but whether this increase helps or hurts a metal's corrosion resistance depends on the specific case. Often, high temperature corrosion results in production of thick continuous scale which covers the metal surface and acts as a barrier to further corrosion. Sometimes, however, this scale is not

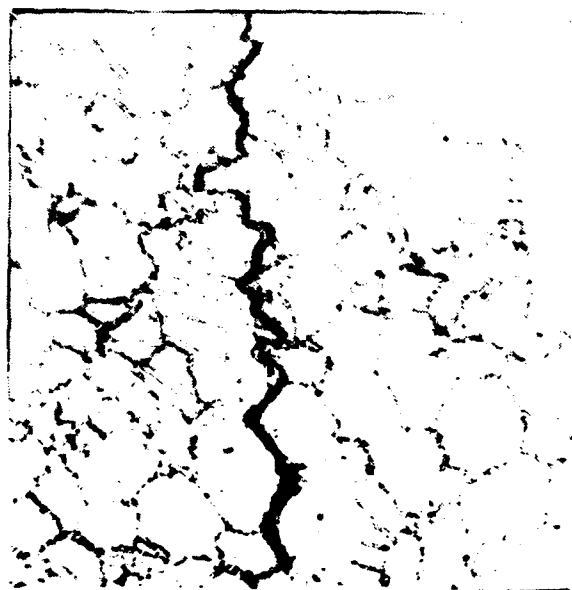


Figure 4-22,

INTERGRANULAR STRESS CORROSION CRACK

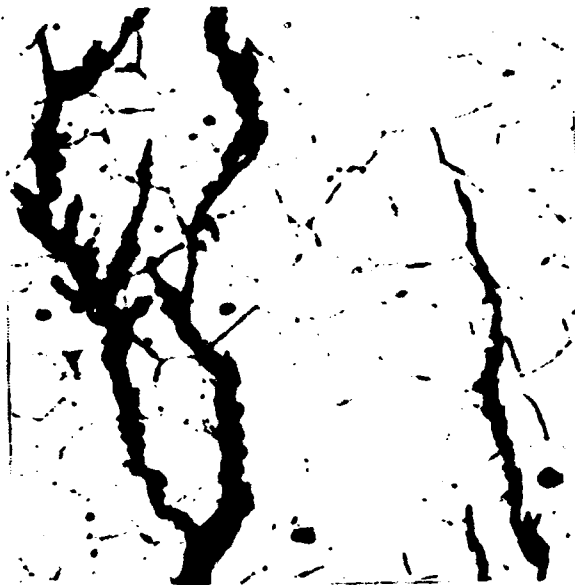


Figure 4-23
TRANSGRANULAR STRESS CORROSION CRACK



Figure 4-24

CORROSION FATIGUE OF COPPER TUBE

continuous, but full of blisters. The oxide layers spall or crack, and further corrosion occurs.

Sulfides, nitrides and carbides also form more rapidly at high temperatures. Serious corrosion problems can arise if concentrations of offending compounds in the environment are not kept low. Often alloying changes can reduce the effects of high temperature corrosion appreciably.

4.13 STRAY CURRENT CORROSION.

4.13.1 General. Stray current corrosion is the result of current (usually man-made) flow through paths other than the intended circuit. While direct current (DC) is generally thought of as the source of this type of corrosion, alternating current (AC) has also been associated with it. Stray current corrosion is electrochemical, as is galvanic corrosion. It occurs where current leaves metal surfaces. This is usually on external surfaces of buried or submerged pipes or cables. However, internal pipe surfaces, in contact with low-resistant fluids mechanically coupled, have also been a problem. Current always takes the path of least resistance back to its source, and metals, being very conductive, are an attractive path. Stray currents will flow from their source through an electrolyte to a metal structure, move along the metal, and return to the source through the electrolyte. Metal will be a cathode where current is picked up, and an anode where it is discharged. Thus corrosion will proceed. (Figure 4-25.)

As with other types of corrosion, stray current can result in severe metal losses. Steel, for example, corrodes at the rate of 20.1 pounds per year for each ampere of current flow. Lead loses 74.5 pounds per ampere-year.

Stray current corrosion does not generally look different than ordinary soil corrosion. Electrical measurements are needed to detect it. Stray current can be detected by measuring structure-to-soil potentials and current flow (IR drop). Structure-to-soil potentials will give indications only when measured in an area of current discharge or pick up. Current flow (IR drop) readings will indicate in between the pick up and discharge areas where structure-to-soil potential would show nothing (paragraph 6.1.2.2.c). Recording instruments and special techniques are required.

4.13.2 Stray Direct Current Corrosion. The many sources of direct stray current can be divided into two general categories: fluctuating or steady. Stray current characteristics (fluctuating or steady) can be observed from charts of recording instruments.



Figure 4-25

STRAY CURRENT CORROSION OF
UNDERGROUND CAST IRON PIPE

4.13.2.1 Fluctuating Direct Current. Fluctuating stray current is leakage from equipment which does not operate continuously or at constant output. Among the most prominent sources are: direct current power systems, electric railways, railway signal systems, direct current industrial generators, direct current mine equipment, elevator motors, direct current welding equipment, electronic equipment that allows direct current components to escape, electric furnaces, electroplating equipment, grounded neutral direct current electrical systems, and "magnetic storms" producing telluric currents.

One frequent cause of fluctuating stray current corrosion is the improper grounding of welding generators used in repair work. The improper and proper grounding of a welding generator are shown in Figure 4-26. When a direct current generator is improperly grounded, corrosion damage can be caused to the underground or underwater metallic structures in the area.

Mass transit systems (subways, surface traction cars, etc.) operate on D.C. with rails returning current. All operating and proposed transit systems let some leakage current get into the ground. (Figure 4-27.) This is because they use running rails for returning current to substations. Fourth rails or overhead catenaries have been ruled out as too costly. However, transit system designers now realize that problems develop and are designing to minimize leakage. All welded and sometimes heavier rails are being laid on high-density concrete ties with rubber padding under the rail. Substations will be spaced approximately one mile apart for the modern subway as compared to a three to five mile spacing for the old surface trolley systems. (Stray current is reduced six times by changing substation spacing from four miles to one mile.) Track cross bonds, for reduction of rail circuit resistance, are normally installed at 2,000' intervals in subway systems.

Stray current from transit systems varies with designs, maintenance procedures, soil conditions, and configuration of adjacent utility structures. One old surface streetcar system is known to permit 10% to 20% of its substation load to return over the city gas distribution system. Old subway systems will lose only 5% to 10% of this amount, while the new ones are expected to leak only 1% to 5%. Substation current capacity is usually around 3,000 amperes for subways and about 1,000 amperes for streetcars.

Underground mining operations produce stray currents in this same way. Mine systems, however, often produce more stray current problems than transit systems. Frequently they are poorly-maintained and constructed or are only temporary operations. Use of inferior materials, lack of bonding, and

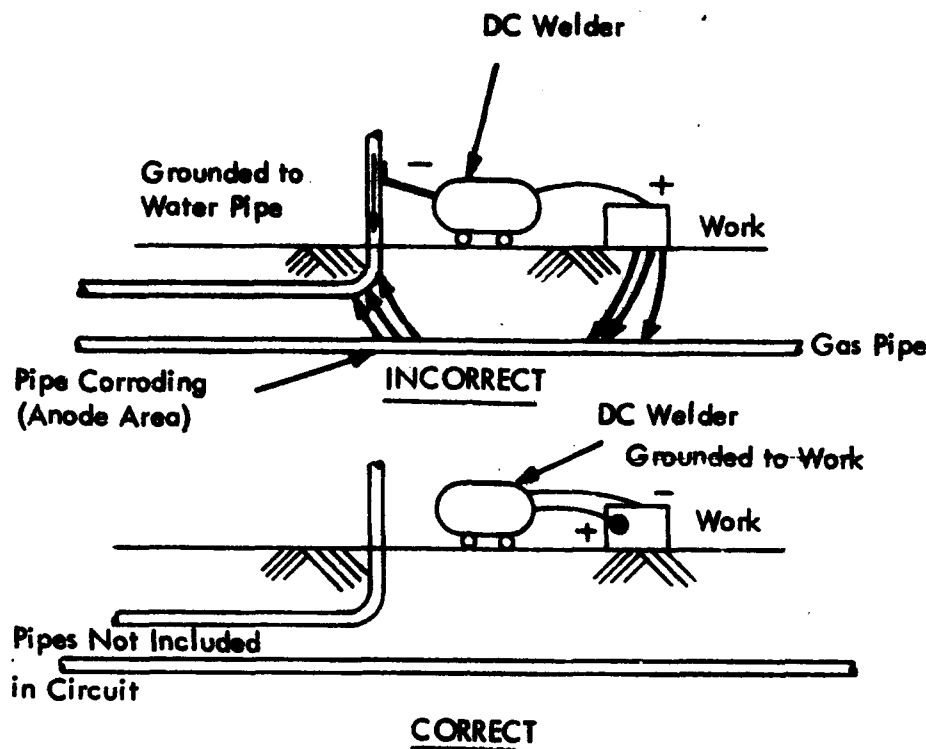


Figure 4-26

CORRECT AND INCORRECT GROUNDING OF WELDING GENERATOR

poor upkeep can result in current leakage greater than 50%. More costly methods of construction and corrosion protection are often not considered because these systems are frequently moved as new mines open up and old sections are closed down. Another cause of serious stray current is connecting mine car rails to the positive terminal, a practice now illegal in many states. This produces stray currents which cannot be drained from neighboring buried structures. When necessary, control of mine system currents is accomplished in much the same way as transit systems.

Another fluctuating stray current, not man-made, is telluric current. These occur during periods of "magnetic storms" caused by sunspots. Variations in the earth's magnetic field at these times induce voltages on underground structures, usually pipes or cables, running east and west. Severe currents of many amperes are possible; however, their duration is usually quite short.

4.13.2.2 Steady Direct Current. Steady stray direct current results from machinery which produces a continuous, constant level of current. Examples are: battery chargers, electroplating, and cathodic protection systems.

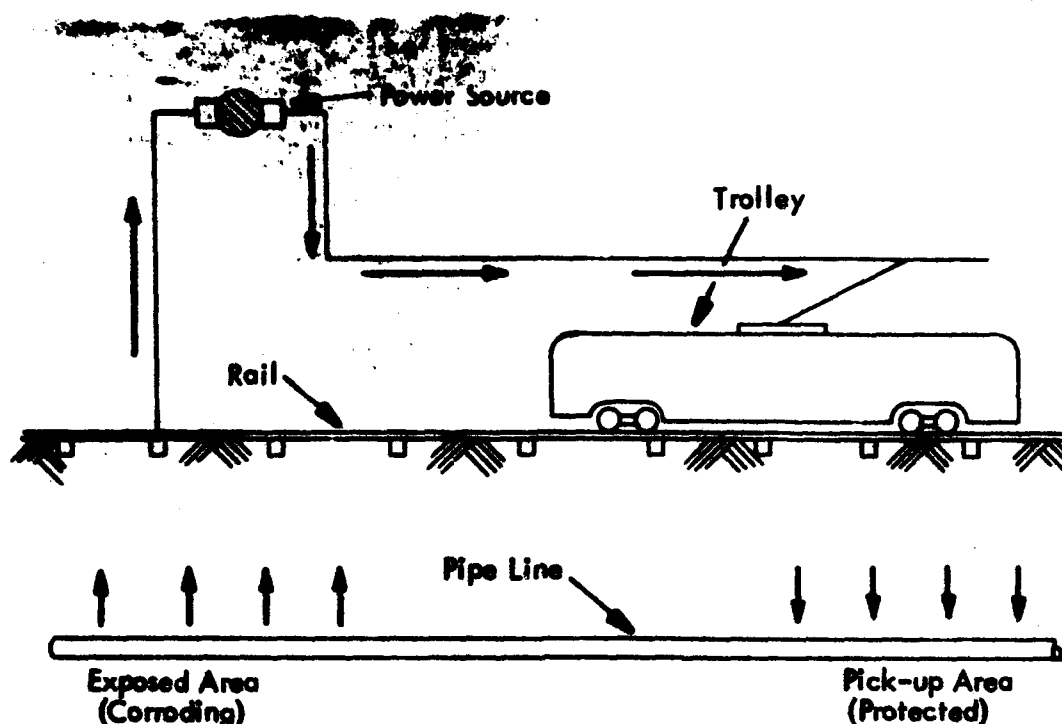


Figure 4-27
STRAY CURRENT CORROSION

Impressed current cathodic protection is probably the most common source, because of its prevalence on cross-country pipelines, gas and electric distribution systems, and the increase in total pipeline mileage. Properly designed cathodic protection will, however, result in no more than 5% or 10% leakage on adjacent structures. This is usually easily mitigated by cooperation between owners.

4.13.2.3 Effects of Direct Stray Current. Severe, localized corrosion can occur where stray direct current leaves a metal structure (Figure 4-28), whether current is fluctuating or steady. (See Table 3-2 for metal losses due to current flow.) In above-ground construction, such as electroplating equipment, particularly when high voltages are used, stray current can be an electrical hazard as well as a source of corrosion. It is difficult to achieve adequate insulation in plating rooms; leakage currents, although a small percentage of the total current, may cause considerable damage, chiefly because the amperage used in electroplating is extremely high. In addition to plating equipment, all the causes previously listed can result in corrosion within buildings. Unfortunately, the resulting corrosion is not necessarily limited to portions of metal structures that are underground. Pipes running through moist walls, column footings, and other structural members may experience



Figure 4-28

FLANGE AND BOLT CORROSION CAUSED
BY STRAY CURRENT ON CAST IRON PIPE

localized corrosion where the current leaves the structures.

Stray current can emanate from within a military installation or from some source external to it. Probably the most frequent source of stray current in either case is impressed current cathodic protection, although direct current welding systems may be severe.

Control of stray direct current is generally most effectively accomplished by drainage bonds (paragraph 5.7). A drainage bond is located at a convenient point, not necessarily at the point of greatest positive structure-to-soil potential change. The required bond resistance can be calculated from field measurements, or established by "trial and error". (paragraph 6.1.2.2.c.) If the "critical" point is corrected by this method to its original potential (reading before stray current flowed), other test points on the same structure will automatically be corrected. Some engineers, who do not like to interconnect pipelines, will install a few magnesium anodes at the "critical" point. This will usually correct only the local area directly opposite the anodes.

Stray direct current problems from cathodic protection systems can be minimized in the design phase (paragraph 7.3.3). Geometric location of anodes with respect to foreign structures is the most important single factor to consider. All companies in an area should cooperate so that complicated problems do not arise. Coordinating committees have been formed in major U.S. metropolitan areas to act as information "clearing houses".

4.13.3 Stray Alternating Corrosion. Corrosion by stray alternating current is a complex phenomenon, not yet fully understood. Stray alternating current produces highly-localized corrosion similar to that caused by direct current, but only a fraction as intense. Stray alternating current is generally thought to produce about 1% as much corrosion as a like amount of direct current. This is the result of the direct current component of alternating current, which reacts with metal as does normal direct current.

Under certain conditions, alternating currents may be rectified in passing through and off a metal structure producing a direct current component. In such cases, stray current corrosion will result. That effect has been found to become less active with time in most reported cases. Damage from partially rectified alternating currents has been found in the vicinity of large substations, central power stations, gas and water distribution systems, and other places where ground currents can be excessively heavy. (reference 7.)

Damage to a lead gooseneck is shown in Figure 4-29. This damage occurred within a month after installation in a heavy ground-current area. It is believed to have been caused by rectified alternating current. Corrosion of aluminum cable submerged in water when subjected to alternating current has been confirmed experimentally in the laboratory. An explanation of this type of corrosion is that during one half-cycle when the aluminum is at negative polarity, sodium hydroxide forms next to the aluminum. This dissolves aluminum's normally protective film and some of the aluminum. During the next half-cycle, the current flows from the aluminum into the electrolyte, thus removing some of the aluminum by electrolysis and partly by re-forming the film. In time, the layer of corrosion products formed maintains an alkaline condition at the aluminum surface in spite of alternation of polarity. This is due to partial rectification of alternating current.

In the absence of current, aluminum is anodic to copper. When immersed in salt water, galvanic current flows from aluminum through the electrolyte to the copper, resulting in the corrosion of the aluminum. When alternating current is impressed between aluminum and copper, the flow of galvanic current will be neutralized by the larger current resulting from partial rectification of the alternating current. Current flow then is from the copper through the electrolyte to the aluminum. This will result in corrosion of copper to aluminum due to partial rectification of the alternating current.

Alternating current induced on well-coated underground structures may also result in stray current corrosion. When overhead electrical transmission lines are located above such a structure, it acts as an induction coil to produce alternating current voltage across the coating. The resultant induced alternating current is a possible cause of corrosion. In addition, it is a safety hazard which should be controlled.

4.14 IDENTIFYING CORROSION AND ITS SOURCES. Determining structural failure cause is often a complicated procedure. Sometimes a failure appearing to be strictly mechanical is actually the result of corrosion.

Corrosion takes many forms, depending on the material, its state, the environment, and the time involved. It may be very localized, confined to a tiny pinhole. Or it may take the form of general deterioration of an entire surface. There may be a weight gain or loss involved. For underground or submerged structures, visual examination may be impractical or impossible; electrical measurements are most often used to locate corroding areas and determine whether or not corrosion is being controlled.



Figure 4-29

CORROSION OF LEAD GOOSENECK
CAUSED BY RECTIFIED ALTERNATING CURRENT

4.14.1 Visual Examination.

4.14.1.1 Macroscopic. Visual examination of a corroded structure can reveal much about the mechanisms and sources of corrosion. The structures should be checked for general appearance, for corrosion products, for pits or cracks or any specific pattern. Metals do not merely "rot"; they corrode because of some unfavorable conditions which, if recognized, may be avoided or overcome to prevent further failures.

a. General Corrosion. General corrosion, or uniform attack, is overall deterioration of a structural surface. There is no distinct, localized area of attack, but a gradual, more-or-less evenly distributed destruction. Although this type of corrosion is probably the most common, it is also relatively simple to deal with. No catastrophic failures are expected, because failure from uniform attack is a function of time. It is relatively predictable and can be dealt with by whatever means is most economical: extra wall thickness, more resistant materials, coatings, insulation, cathodic protection, or others.

b. Pitting. Pitting is localized attack which produces cavities in the metal surface. These cavities begin at the surface and sometimes fill up with corrosion product, forming mounds. These mounds or "tubercles" (Figure 4-30) can be removed chemically or physically to reveal deep pitting underneath. The pits themselves are generally roughly hemispherical or conical in shape. Sometimes they are angled from the perpendicular; often, they are not.

This attack is especially dangerous because perforation can result even though little corrosion has occurred overall. (Figure 4-31.) Perforation can be an expensive problem, resulting in leakage and equipment failure.

Pitting goes through four stages on a metal surface: (1) initiation, (2) propagation, (3) termination, and (4) re-initiation. Pitting usually initiates on a metal surface covered with a thin, adherent film. Pits develop at breaks or weak points in the film, these points being naturally anodic to the remaining surface (Figure 4-32).

The pit propagates at a rapid rate, due to alterations in the environment. As a result of corrosion, the region surrounding the anode (pit) area becomes more acidic while that surrounding the cathode becomes alkaline. Because of the "area effect" (large cathode and small anode), the penetration rate is quite high. However, this decreases with time, as more pits form and the relative areas become more similar. Pitting terminates for many reasons: filling up the cavity with corrosion product, drying out of the surface, changes in the environment, etc. Re-initiation occurs as the result of similar, but opposite changes.



Figure 4-30

TUBERCLES ON INTERIOR OF HOT WATER TANK



Figure 4-31

PITTING FAILURE OF 8-INCH FIRE MAIN
(CHALK-MARKED PITS LOCATED ON PIPE BOTTOM)

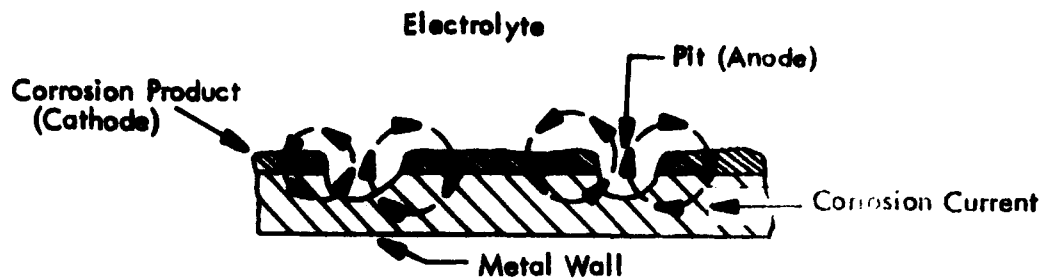


Figure 4-32
PITTING CORROSION

Stray current also can produce pitting. In fact, wherever a current leaves a metal surface, pits may appear. Galvanic cells of all sorts fall into this category, and stray current corrosion cannot normally be identified as such visually.

Impingement of entrained solids or gases in a moving liquid stream can damage a metal's protective film and produce deep, angled pitting. Cavitation can do likewise, as the shock of implosion breaks up the film.

Pitting may occur in crevices or stagnant areas where concentration gradients exist in the environment (Figure 4-33). It is frequently observed in stainless steel, copper, aluminum, magnesium and titanium as a result of their surface films. Pitting of other metals occurs under circumstances discussed above. Treatment of this problem may require changing to a less susceptible metal or altering the specific conditions depending on the sources.

c. Cracking. Cracking of metal due to corrosion generally falls into one of two categories: stress corrosion and intergranular corrosion. Stress corrosion, discussed previously (Figures 4-22 and 4-23), is the result of combined tensile stresses and corrosive surroundings to a susceptible alloy. It is generally thought that pure metals are not subject to this type of destruction. Cracks form either inter- or trans-granularly, and may fluctuate from path to path. Aluminum alloys, brasses, and low-carbon steels generally exhibit intergranular stress corrosion or cracking. Other metals, especially the 300 series stainless steels, crack transgranularly.

Intergranular corrosion is selective attack following a path along the grain boundaries of the metal. Individual or groups of outer layer grains may drop out of the structure; tensile strength decreases, and surface cracking is apparent.

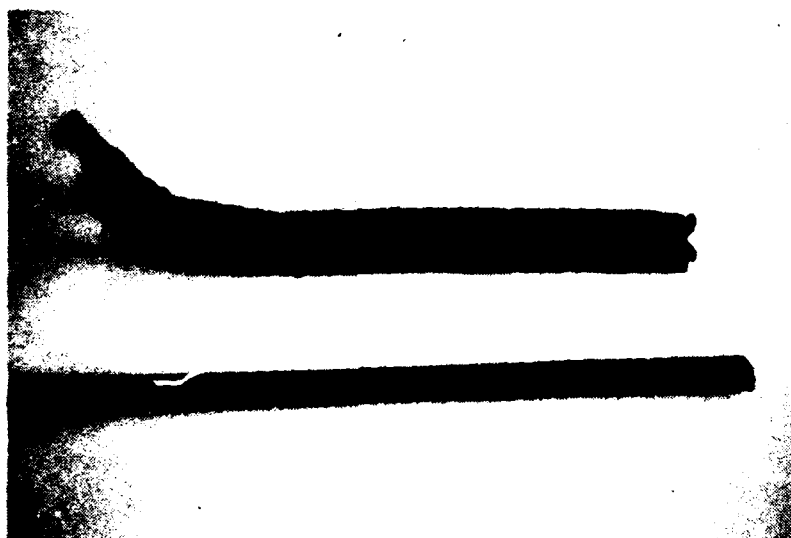


Figure 4-33

PITTING OF PIPE AND METAL SUPPORT BY FATTY ACIDS

The mechanism of this attack is galvanic; a potential difference develops between the grain and its boundary. The difference may be one of chemical composition caused by cold work or heat treatment of the metal. Grains are always under slightly different stresses than their boundaries. Therefore, cold working or heat treating metal can result in migration of an alloying element or impurity from the grains to grain boundaries. Precipitation there may result, producing a potential difference between the two regions. If precipitate is anodic to the remainder of the grain, intergranular corrosion will proceed along the path of the impurity. If the precipitate is cathodic, cracking occurs in the region immediately adjacent to the boundary. Intergranular corrosion is most often observed in the 18-8 stainless steels, in aluminum, and copper alloys.

Once cracking is observed by visual examination, the microstructure should be analyzed to determine the type of cracking that has occurred. (Figure 4-34.)

d. Corrosion Reaction Products. A visual examination of the products of corrosion reactions can often be helpful in determining the cause. Different products may result from different sources; a lack of product also reveals much about the mechanism of deterioration. The spatial distribution of a corrosion product may indicate the source of the problem, as in the case of knifeline attack of a weld. However, final analysis of corrosion products usually must depend on more sophisticated means of analysis, such as X-ray diffraction.

Visual examination of ferrous metal under cathodic protection can often reveal if adequate protection has been achieved. Without protection, ferrous metals form the reddish corrosion product ferric oxide (rust). Cathodic protection current chemically changes this compound to black ferrous oxide (magnetite). This color change is often apparent.

4.14.1.2 Microscopic. Microscopic analysis of a corrosion failure can add much to the picture formed by visual examination. Metallographic analysis is probably the most helpful laboratory technique for determining the cause of failure. The path of cracking, whether intergranular or transgranular, may be revealed. Impurities on the metal surface can be located, and improper heat treating or excessive cold working can be discovered. Other defects in the microstructure which may have influenced corrosive tendencies can be analyzed.

Electron microscopy and X-ray diffraction may be employed to determine the composition of reaction products. Other sophisticated techniques are used also, but to a lesser extent, to help find the cause of actual failures.

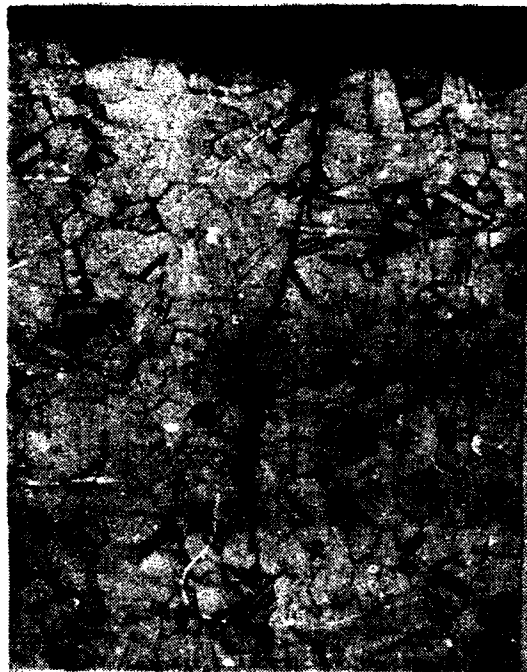


Figure 4-34

TRANSGRANULAR BRANCHING CRACK
ORIGINATING FROM TUBE ID

4.14.2 Loss of Metal. Corrosion is usually accompanied by a net gain or loss of weight, as metal is deteriorated and perhaps replaced by corrosion products. When analyzing a corrosion failure, the products of reaction are removed, and the weight loss is measured as an indication of corrosion rate.

Loss of metal is usually measured one of two ways. Either the weight loss per unit area per unit time is determined; or the loss of metal thickness (depth penetration) per unit time is found. The former is commonly taken in units of mdd (milligrams per square decimeter per day); the latter, in mpy (mils per year). It is debatable as to which method of recording metal loss is more appropriate. The former applies well in situations where uniform attack prevails. The latter is much more applicable in measuring localized corrosion, i.e. pitting.

4.14.3 Statistical Analysis. Statistics on failure rates of any structures can determine whether corrosion or physical damage is responsible. Once corrosion reaches the point where failures occur, rate of failures increases each year. Experience has shown that corrosion failures increase logarithmically (references 8 and 9). Failures due to causes other than corrosion will not usually exhibit this curve but, generally, follow a straight line curve (Figure 4-35). Here, each failure has been examined and logged as due to corrosion or noncorrosive causes. Corrosion breaks continue to increase, while breaks due to noncorrosive causes remain almost constant. An increase in the rate of noncorrosive breaks occurred in 1961. The curve before and after 1961, however, is still linear. The overwhelming influences of corrosive failures cause the total leak curve (failures due to corrosive and noncorrosive causes) to assume the logarithmic slope.

Statistical analyses can be especially useful in corrosion of cast iron pipes, where corrosion failures are generally the result of graphitization (paragraph 4.5). Here, escaping water may wash away the graphite leaving no evidence that corrosion caused the break. A record of breaks exhibiting the characteristic logarithmic shape will reveal corrosion as the true cause.

4.14.4 Electrical Measurements. Electrical measurements are employed to predict a potentially corrosive situation, and have actually located failures underground. Corrosion surveys, to determine environmental (soil or water) pH and resistivities for proposed structures can help indicate what materials should be used and whether corrosion control such as coatings and cathodic protection will be needed. When a new metal - environment combination

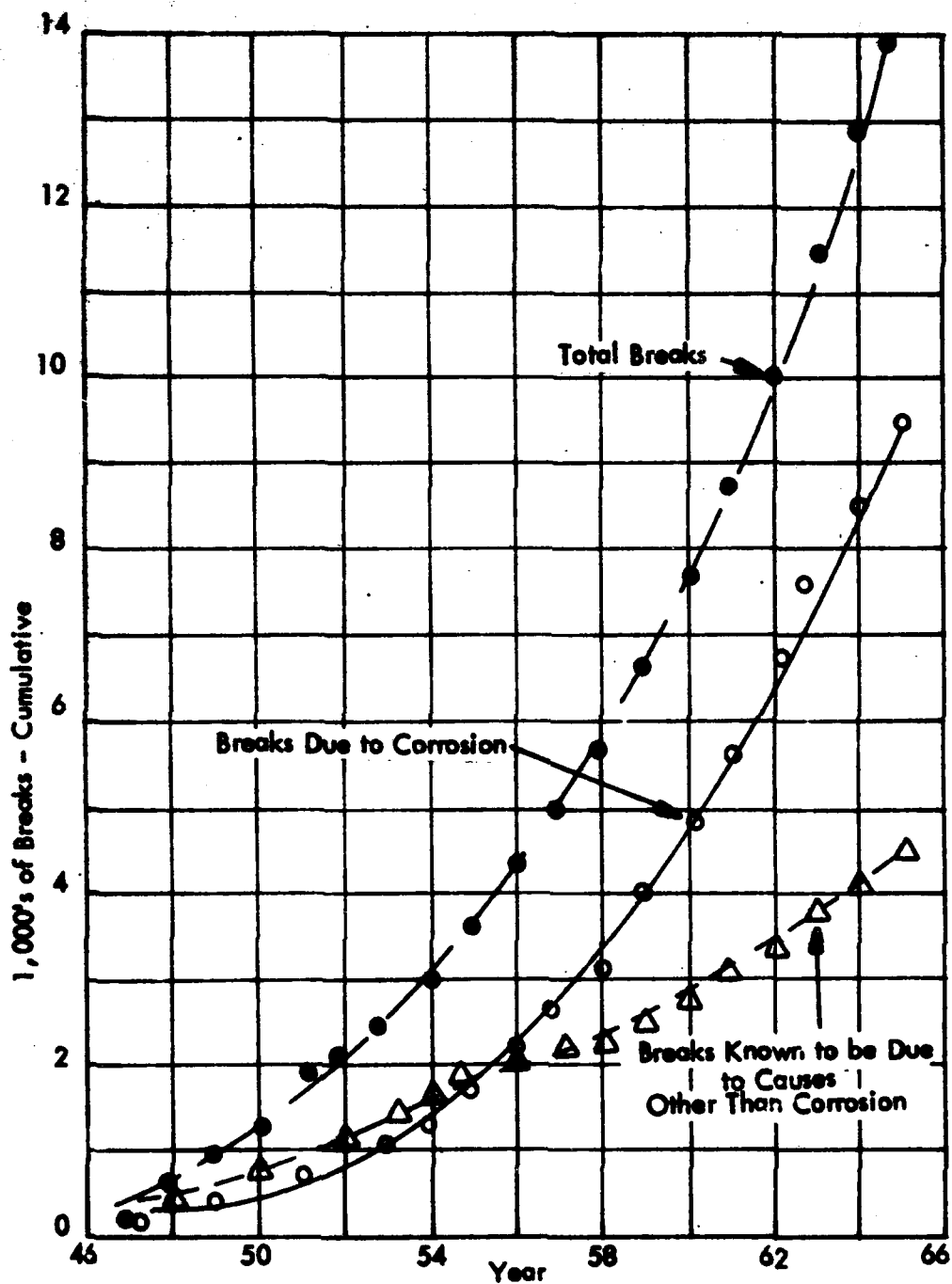


Figure 4-35

COMPARISON OF BREAKS DUE TO CORROSIVE AND NONCORROSIVE CAUSES

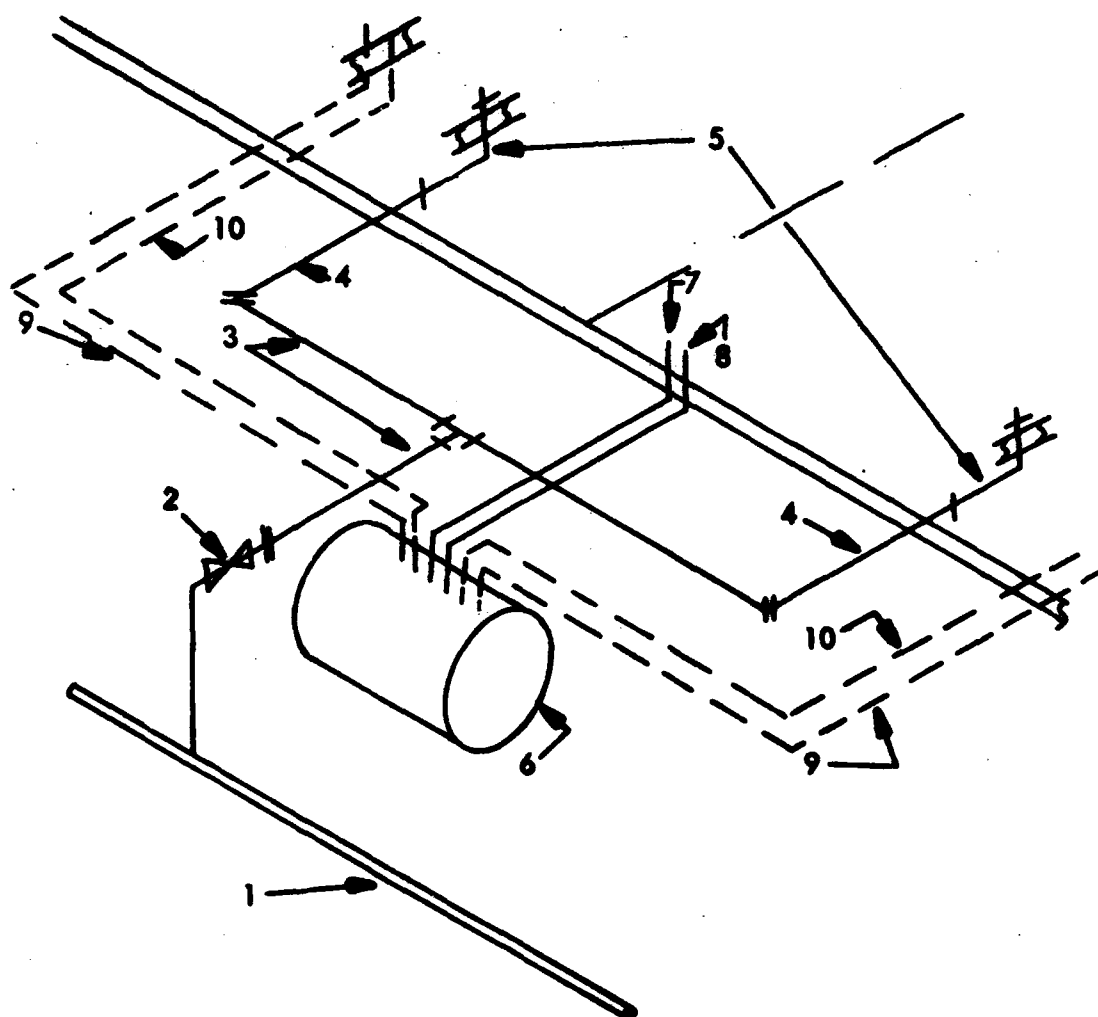
is expected for which no corrosion behavior data is available, laboratory electrical tests can be helpful. Where uniform attack is expected, a sample of a metal in the form of a wire is immersed in the corrosive environment. As it corrodes, its cross-sectional area decreases. Since electrical resistance in a wire is an inverse function of cross-section, a measure of the increasing resistance indicates the rate of corrosion. This procedure is possible in electrolytes other than liquids and is relatively simple. Problems arise if conductive reaction products form on the test specimen, affecting the real cross-sectional area.

Field (job-site) electrical measurements on existing structures can indicate where corrosion is occurring or expected. Potential and line current surveys can reveal the extent to which corrosion has progressed, stray currents, the location of "hot spots", and if electrical continuity exists. A complete discussion of corrosion survey techniques is found in Section 6.

4.14.5 Chemical Analyses. As mentioned before, X-ray diffraction and electron microscopy can be employed to study the composition and structure of reaction products. Other techniques such as X-ray fluorescence, electron-probe microanalysis and spectrographic analysis may also be considered. In all of these methods, surface contamination of the metal can greatly interfere with a correct analysis. Also, variation in product composition from point to point can adversely affect the study.

Chemical analysis of the corrosive environment can reveal the source of corrosion. Determination of soil pH and the presence of sulfates (indicating anaerobic bacteria) is generally included with corrosion survey measurements to give a more complete picture of environmental corrosivity. Where water is the environment or is carried in pipes, analyses of water composition - dissolved solids and gases, hardness as calcium carbonate, and pH - can indicate possible sources of corrosion.

4.15 SPECIFIC MILITARY PROBLEMS. A military installation, like a city or industrial complex, commonly experiences corrosion in many forms. Frequently, bases have been built in a hurry, during times of crisis, with no thought to corrosion control. A variety of metals, interconnected without insulation or other corrosion control measures, is common in existing bases (Figure 4-36). Often it is not practical or economical to protect all structures which are corroding. Some should be replaced, when failure occurs, with better materials and better engineering, to prevent future problems.



- | | |
|--|---------------------------------|
| 1. Cast iron water main | 6. 550 gal. steel fuel oil tank |
| 2. Brass service stop & copper nipple | 7. Galvanized steel filler pipe |
| 3. Galvanized steel service & header | 8. Galvanized steel vent pipe |
| 4. Copper water line - under slab | 9. Copper suction line |
| 5. Galvanized steel elbow - through slab | 10. Copper return line |

Figure 4-36
VARIOUS METALS AT TYPICAL MILITARY BASE

Others, where the mission or economics dictate, require corrosion control without repair or replacement.

Proposed structures should include corrosion control as part of their design. This avoids additional expenditures and inconvenience caused by repairs and failures. Military structures commonly experiencing corrosion problems are analyzed here. A discussion of corrosion control is included in paragraph 5.

4.15.1 Service Lines. Water, gas, and oil lines (usually buried or submerged), servicing military installations, corrode for many reasons. Often various metals are interconnected producing galvanic corrosion. Other conditions may corrode metals, usually ferrous or copper, used for these applications.

4.15.1.1 Copper Lines. Copper is often considered relatively inert to corrosion. However, copper service lines often experience external corrosion in the atmosphere or in some soils, especially where they are not interconnected with ferrous metals. Internal corrosion may occur in domestic copper water lines. In the atmosphere, copper develops a thin external coating or patina of corrosion products (mainly copper sulfides) from reaction with sulfur dioxide. Once formed, this patina generally protects copper from further atmospheric corrosion by acting as a barrier.

Underground, copper lines are resistant to corrosion in most soils. Exceptions are highly alkaline soils and those containing organics in great amounts.

Another cause of corrosion in underground service lines, especially copper, is lawn fertilizer. Nitrates and other corrosion compounds make fertilizers aggressive to metals. Underground copper lines to houses are often run fairly close to the surface, and fertilizers can easily wash down to the level of these pipes. In addition, since copper is attacked by sulfur compounds, marshes and cinder-bearing soils are unacceptable environments.

Copper receives cathodic protection from ferrous metals, when connected to them. When copper is not connected to ferrous metals (if all copper or copper and plastic lines are used), no protection is received, and copper may corrode. It is then often thought that corrosion resulted from environmental conditions in which copper had not been tested previously, when actually it occurred because no ferrous metal was present to provide cathodic protection.

Copper water lines are subject to internal attack under certain conditions. Obrecht and Quill (reference 10) have

shown that conditions of water quality, velocity, and temperature can produce erosion-corrosion in copper and copper alloy distribution systems. For aggressive waters, temperatures above 140°F and velocities above 4 feet per second in copper piping result in cavitation erosion (paragraph 4-7), deep, spongy pitting of the metal accompanied by absence of copper corrosion products. For less aggressive waters, 8 feet per second is the critical velocity. This effect is magnified at high turbulence areas such as couplings.

When water velocities and temperatures cannot be maintained under specified limits, modifying water quality can reduce cavitation. Soft waters are more aggressive than hard waters. Altering pH with sodium bicarbonate or sodium hydroxide will make soft waters less aggressive by increasing their scale-forming tendencies. Another possibility is removing dissolved carbon dioxide and oxygen. Other chemical treatments may be required in specific cases. Overly high velocities and temperatures should be avoided in design. Expansion of facilities or addition of high temperature equipment (industrial dishwashers, laundries) often requires new distribution system designs because of increased load - temperature and velocity - on existing lines.

4.15.1.2 Steel. Steel and galvanized steel pipe are used in gas, oil and water distribution systems. Corrosion of these materials occurs in many environments encountered in military projects. One common situation is the galvanic cell between steel and other materials such as copper (paragraph 4.2.1). Severe corrosion of steel adjacent to other metal often results. Use of proper insulation or other corrosion control can prevent this. All ferrous metals - steel, cast iron, etc. - corrode at approximately the same rate. Steel lines often fail more rapidly than cast iron, however, because their walls are thinner. Also, since steel does not contain free graphite like cast iron, graphitization, where the metal corrodes leaving a weakened but often still solid structure, cannot occur. When steel corrodes, the walls thin or pit. (Figure 4-37.)

Steel lines in soils may often corrode. Differential environment conditions can produce pitting or general corrosion. Oxygen concentration cells may induce severe corrosion on bottom surfaces. Organic material - leaves, wood, etc. - in soil feed sulfate-reducing bacteria which are known to cause failure of ferrous metal. Cinders and other impurities will also produce corrosion. Galvanized steel receives some protection from its zinc coating; however, these coatings are thin and do not last long underground. Above-ground may provide adequate protection, but nonmetal coatings and cathodic protection are often needed underground to insure the life of steel service lines. Steel



Figure 4-37
PITTING OF STEEL LINE - SOIL CORROSION

lines in water may also require such corrosion control.

Galvanized steel is often used for water service lines. It serves well below about 140°F. Above this temperature, the relative potentials of steel and zinc begin to reverse. Above 170°F, steel corrodes, protecting zinc galvanizing.

Low alloy steels carrying domestic soft waters will corrode forming pits and tubercles of rust which block the inside diameter. In semi-hard waters (containing calcium carbonate) and those containing some carbon dioxide, protective films form restricting or eliminating corrosion. Water quality may be altered by chemical treatment to produce these films in many cases. Cathodic protection has also been applied successfully for special applications. Higher levels of carbon dioxide may be corrosive. To determine proper calcium carbonate levels, the saturation index for the subject water must be determined (water analysis).

Stainless steels are generally resistant to water corrosion, but will fail when chlorides are present. Sea water will damage these steels seriously, causing pitting and overall deterioration.

In general, velocity increases corrosion in steel lines. Cavitation erosion occurs in steel at various velocities, depending on water quality.

4.15.1.3 Cast Iron. Cast iron lines form internal pits and tubercles to about the same extent as low alloy steels in water service. Water treatment is usually the solution with these materials, also. External corrosion in soils and waters, however, occurs under less severe conditions, although the corrosion rate is the same. In addition, graphitization of cast iron in gas lines as well as others can be a serious corrosion problem (paragraph 4.5).

Care should be taken to assure electrical continuity across joints. Mechanical and rubber slip joints do not provide this. The best joint bond consists of a length of No. 2 or 4 insulated copper cable thermit-welded across the joint. (paragraph 5.7.) Joint bonds are required when cathodic protection is installed, but they are a good idea otherwise, also. If bonds are applied when the pipe is installed, the cost of future cathodic protection is greatly reduced (excavations, etc. required for bonding). Additionally, in stray current areas, bonding prevents these currents from going around each joint, producing corrosion wherever current leaves the metal.

4.15.2 POL Facilities and Hydrant Refueling System. POL facilities are among the most important military structures because their continuous operation is necessary to

performance of the mission. Fuels carried in these facilities are highly-flammable and, therefore, leaks present a safety hazard. For these reasons, corrosion control of POL facilities is often necessary even when repair costs do not justify it. However, underground structures such as hydrant refueling lines are often located beneath concrete, making repairs difficult, inconvenient, and expensive.

Metals most commonly encountered in POL facilities include steel, copper, and aluminum. As with service lines, galvanic cells must be avoided. Steel pipe and underground tanks usually require coatings and cathodic protection to protect them from soil corrosion. Above-grade tank bottoms resting on the ground may still corrode when resting on sand or oiled-sand bases and may require some form of protection.

Copper in service of this type (because of its interconnection with steel) usually is not much of a problem. General precautions to consider when using copper are covered in paragraph 5.3.2.6.

Aluminum alloys are fairly reactive but form a protective oxide film in many environments. Corrosion of aluminum is discussed in paragraph 5.3.2.5. In POL and other facilities receiving cathodic protection, care must be taken not to overprotect aluminum structures. Alkaline reaction products from excess cathodic protection may corrode aluminum seriously, as will alkaline soils. Aluminum should not be allowed to contact concrete and should be kept away from limestone fill.

4.15.3 Fasteners. There are several likely sources of corrosion of metal fasteners (bolts, nails, straps and so on). First, galvanic cells can result when fasteners are made from metals different than the main structure. The more anodic metal, either fastener or metal structure, will experience increased corrosion. Since fasteners have small surface area compared with the remainder of the structure, the "area effect" (paragraph 3.2.3.3.a) is important. It is more desirable from a corrosion standpoint to have a large anode (structure) and small cathode (fasteners) than the opposite. Use of fasteners made of metal like the structure or dielectric insulation are among the ways to mitigate this problem. Coatings and cathodic protection are also used.

Failure of fasteners themselves can result from improper heat treatment after fabrication. Internal stresses combined with corrosive environments may produce stress corrosion cracking. Also, stressed areas or bright metal, such as screw threads or nail heads and points, are anodic to the remainder of the fastener. These areas will experience increased corrosion because of the galvanic cell arising.

Proper heat treatment to relieve stress can control these problems during fabrication.

4.15.4 Pipeline Casings. From the corrosion control standpoint, casings should not be used. Kuhn and others (references 11 and 12) show that casings introduce two major corrosion problems:

1. Short circuits developing between casing and carrier pipe make cathodic protection of enclosed pipe impractical.

2. In unprotected lines encased in lower quality metal, short circuits set up galvanic cells between casing and carrier pipe.

The first problem may result because end seals may never actually seal. Moisture can leak through, and the annular space between casing and carrier pipe will at least partially fill with ground water. Condensation can be a problem even if a fairly good seal is obtained. Unless the carrier pipe inside the casing is cathodically protected, serious corrosion occurs. The casing itself, if insulated from the carrier pipe, can be utilized to conduct cathodic protection current to the carrier pipe; but only if it is not well-coated. If a carrier pipe is shorted to a casing (a common situation with long spans of pipe), only the external surface of the casing will receive cathodic protection. The exterior of a bare, insulated casing will pick up part of cathodic protection current designed for the carrier pipe and discharge this current through the electrolyte in the annular space. This will provide cathodic protection to the carrier pipe. A well-coated, insulated casing will have a significantly higher resistance to earth than the relatively long carrier pipe. This coated casing will pick up only a minute portion of cathodic protection current, insufficient for cathodic protection of encased carrier pipe. The carrier pipe will prevent insulated, coated casing from receiving adequate current in the same manner a short-circuited, bare casing prevents its coated carrier pipe from receiving adequate protective current.

Casings can short circuit to carrier pipes for such reasons as vibration, settlement, etc. Then, cathodic protection of carrier pipe inside casing is impossible. With a well-coated casing, the carrier pipe inside the casing will have no cathodic protection. With bare casing, not only the portion of carrier pipe inside the casing will lose cathodic protection but cathodic protection for large distances on both sides of the casing will be seriously reduced or rendered ineffective. Cathodic protection current will not seek holidays in carrier pipe coating but will flow to the large, bare, low-resistance casing. Thus, casing is effectively a bare portion of pipe.

The second problem may occur because casing material is frequently lower quality steel than carrier pipe. Short circuits between the two can result in galvanic cells, increasing corrosion and contributing to eventual leaks. This accelerates if the carrier pipe is coated and anodic, due to the "area effect" (paragraph 3.2.3.3.a).

To avoid these problems, pipeline casings should not be used, unless required for safety or mechanical reasons. If a casing is required by codes, a bare casing should be used. Plastic spacers, casing insulators, and end seals should also be installed, and the entire installation should be thoroughly tested and inspected.

4.15.5 Wells. Water wells may corrode for several reasons. Stray currents are often encountered. Because of the length of well casings, gradients exist along its surface. (Several soil strata traversed.) Temperature differentials, differential aeration, and nonhomogeneous soils are likely to affect the casing. Delivery piping, turbine, and strainers may also corrode. In uncased wells, galvanic or impressed current anodes can be used. Protection of cased wells is more difficult. As with pipeline casings (paragraph 4.15.4), well casings are impractical or impossible to cathodically protect; current travels along the casing and discharges into the soil. Protection might be accomplished by using the casing as an anode, corroding it to protect internal structures. Wells or casing embedded in concrete are not immune from corrosion. Concrete, like other coatings, is not perfect and corrosion will concentrate at breaks in the concrete. However, cathodic protection current requirements may be less.

4.15.6 Snow Melting Pipe and Radiant Heating. Snow-melting or radiant heating pipe is usually steel, embedded in concrete sidewalk, floor, etc. (However, copper and wrought iron are often used.) High-temperature water below the boiling point (212°F) circulates, heating the concrete. These systems are often used to melt snow or to heat large structures such as hangars.

Internal corrosion problems similar to those encountered in other steel hot water systems may occur (paragraph 4.15.1.2). External corrosion due to differential environments, however, is the most frequent problem. Steel in concrete, an alkaline environment, is cathodic to steel in soil. Consequently, corrosion occurs at breaks or expansion joints in the concrete, or where the pipe is not completely encased in it but comes in contact with soil beneath. (Figure 4-38.) If the pipes could be completely encased, corrosion would be minimized. Cathodic protection can be successfully applied to protect bare pipe at breaks



Figure 4-38

CORROSION OF RADIANT HEAT PIPE
SOIL - CONCRETE CELL

or expansion joints. The practice of installing polyethylene sheets beneath concrete-encased pipes to prevent contact with soil introduces other problems and should not be followed. Polyethylene sheet prevents moisture from draining into the soil, trapping it. Corrosion of heating pipe may result. Cathodic protection of these lines becomes impossible because of the plastic sheet, so corrosion will continue. A better method of minimizing soil-concrete cells is the use of non-metal chairs or brackets. These support the pipes above the soil while concrete is poured and hardens, surrounding the lines. Non-metal brackets eliminate possible galvanic cells which metal supports could cause.

4.15.7 Caustic Problems. Caustic soda (sodium hydroxide) and other alkalis are not particularly aggressive at normal temperatures, in terms of overall attack. Addition of 1 to 4% caustic to water actually decreases corrosion of steel. Concentrated caustic at high temperatures, however, can produce a serious form of hydrogen embrittlement - caustic embrittlement - in many stressed metals.

Caustic embrittlement is encountered in riveted steam boilers where sodium bicarbonate has been added to the feed water as a corrosion inhibitor. It decomposes with heat to form caustic soda which concentrates at the riveted seams as steam escapes. Concentrations as high as 40% are common there, often resulting in corrosive failure of the metal.

Type 300 series austenitic stainless steels are especially susceptible to caustic embrittlement. Brass also fails this way in ammonia. Besides the cracking typical of caustic embrittlement, serious pitting may also occur. This may occur in boiler tubes during periodic shutdowns if they are allowed to air dry, concentrating the caustic.

Nickel and nickel alloys exhibit resistance to caustic attack and are suitable for use in most conditions. Carbon steel is often used for boilers below 850°F. With proper engineering, to avoid escaping steam, caustic embrittlement problems should not occur.

4.15.8 Stress Corrosion of Various Structures. Stress Corrosion is discussed in paragraph 4.10. Specific military structures which are susceptible to this type corrosion are analyzed here.

4.15.8.1 Fittings. Residual stresses built up in machining metal fittings can institute stress corrosion in slightly corrosive environments. These stresses remain in the fitting unless annealed after fabrication. Improper size fittings forced into place can also develop adequate stresses. Another source of stress is corrosion product build-up between surfaces. These produce stresses, because

they are more voluminous than the original metal. Corrosion products may result from galvanic couples, general corrosion or other, and need not be present in large amounts.

Specific environments in which these tensile stresses produce stress corrosion cracking depend on the metal involved. Aluminum in marine or industrial atmospheres, steels in caustic solutions or chlorides, nickel in hydrofluoric acid or hot caustic frequently experience stress corrosion.

4.15.8.2 Stainless Steels. Stress corrosion cracking of stainless steels is a common occurrence (paragraph 4.10). The type 200 series (16 to 18% chromium with about 5% nickel and some manganese) and Type 300 series (17% or more chromium and 7% or more nickel) are especially prone to this type corrosion. Failure due to stress corrosion in water containing chlorides was discussed in paragraph 4.10. This is probably the most likely cause of failure on a military base, as it is encountered in water distribution or recirculating systems. Crevices where chlorides can concentrate should be eliminated to prevent stress corrosion. Also, chloride and oxygen content in recirculating systems can be kept to one ppm or below.

The Type 400 series (12% or more chromium) may fail by either stress corrosion cracking or hydrogen embrittlement. These steels can be heat treated (hardened) to increase their resistance to stress corrosion. Hardened steels, however, are more susceptible to hydrogen embrittlement.

4.15.9 De-Alloying (Selective Dissolution). Selective dissolution (paragraph 4.5) is probably most common in cast iron lines. Graphitization of cast iron, whether plug type or overall, produces a weakened structure which may give continued good service until a sudden surge or other stress breaks through the weakened structure. A failure of this type is usually characterized by a large hole. The pipe responds with a dull sound when struck with a metal object and may be penetrated easily by a screwdriver. It appears in good condition, but will shatter, or break when pressure surges or water hammer occurs. Statistical analyses of failures occurring in cast iron pipe (paragraph 4.14.3) can also reveal graphitization. (This may not easily be distinguished from mechanical failure.)

Dezincification of brass (paragraph 4.5) may occur in POL facilities where this material is sometimes used for pipe.

4.15.10 Atmospheric Effects. Corrosion of metals in the atmosphere is covered in paragraph 5.3.1.1.a. This is the most prevalent type corrosion, although its severity is not necessarily great. Control of atmospheric corrosion is

accomplished by using resistant metals (paragraph 5.3) and/or applying protective coatings. For detailed discussion of military procedures in this area, see Military Paints and Protective Coatings Manuals.

4.15.11 Water Tanks. Residential hot-water heater tanks, elevated municipal-type cold-water tanks, and others experience internal corrosion. Galvanized steel, the traditional material for hot-water heaters, corrodes at the elevated temperatures required for dishwashers and laundry facilities. Below 140°F, the zinc coating cathodically protects the steel tank. Above 170°F, however, the potentials are reversed, causing accelerated corrosion of steel. Solutions to these problems include the use of coatings and magnesium anodes (cathodic protection) for galvanized tanks, or substituting copper or Monel for galvanized steel. An example of a hot-water heater cathodic protection system is found in paragraph 7.6. Large volume hot-water tanks may require impressed current cathodic protection, because of the greater surface areas involved.

Elevated water tanks are subject to various temperature and climatic conditions. Internal coatings and cathodic protection provide the best solution to corrosion problems. Corrosion is generally most in warmer weather. Tanks in which ice forms experience little corrosion during winter. Cathodic protection design for elevated cold-water tanks depends on tank configuration, including support structures and risers. Examples of this are found in paragraph 7.6.

Special corrosion problems plague tanks holding demineralized (deionized) water. This water, frequently used in producing supercritical steam, is purified in ion-exchange resin beds. Here chlorides, caustics and other undesirable salts are removed. Blistering of internal coatings is worse in demineralized water than in fresh or salt water. Additionally, this type water will not form protective carbonate films on the metal surface, because carbonates are not present. It does, however, tend to dissolve metals. This occurs because the demineralized water is not saturated with any dissolved particles, but often does contain oxygen. Since saturation is a favorable (low-energy) state, it will dissolve whatever it can - the metal surface.

Cathodic protection usually cannot be used, because undesirable impurities are produced. Ordinary coatings are also unsatisfactory, because no coating is perfect. Corrosion would concentrate at holidays and be unchecked with no cathodic protection. The best solution is all plastic equipment - tanks and lines - or rubber inner "bags" for tanks.

4.15.12 Power and Communications Cable. Cables are either "buried" (direct burial in soil) or "underground" (pulled into fiber, vitrified clay, or concrete ducts and often embedded in concrete below grade). Either type construction becomes involved with corrosion of the cable sheath.

Underground sheath cable, exposed to external corrosion, include electric power and lighting cables, telephone, fire alarm, and teletalk cables. The usual construction is the underground method, most commonly providing separate duct runs and manholes for various cable systems. However, some older systems may use common manholes and duct runs.

Corrosion of lead sheath cables is due to several causes, including:

1. Small anodic and cathodic areas of lead due to splices, scratches, and abrasions.
2. Alternate wet and dry duct runs.
3. Galvanic effects due to copper bond straps, ground connections, or proximity to other metals.
4. Stray current effects from electrified railways, industrial chemical operations, and other sources.

In many known corrosive locations, past practice has been to use a protective neoprene sheath over lead sheath to prevent sheath corrosion. This is sometimes satisfactory against local cell action, dissimilar soil environment, and galvanic cells. The stray current problem, however, requires a complete study resulting in the proper use of insulating splices and possible polarized forced drainage bonds. Neoprene sheath construction has proved satisfactory as a moisture-proof coating that apparently has a relatively small deterioration with age. Polyethylene coatings also are reported satisfactory. One incident is known where termites have eaten through polyvinyl chloride insulation on buried cable in North Carolina, resulting in cable failure from moisture seepage.

Insulated jacketed cable on the one hand requires adequate grounding because none will be obtained as a result of the underground cable run. Bare lead sheath cable on the other hand will have a fairly low ground resistance as a result of wet ducts and low soil resistivity. To this is added a grounding system to insure a low ground resistance value. Lead is often coated with tar and wrapped in jute. This type system has a structure-to-soil resistance comparable to coal-tar coated pipe. The grounding system will generally consist of a bare copper ground bus of 500,000-circular-mil size or larger located in a spare duct or embedded in the concrete envelope of the duct runs. Another usual practice is to locate terminal and switching equipment in underground vaults with a considerable ground mass, all of

copper, located at the vault. Both the lead sheath and the copper ground rods and interconnecting cables are bare. A low resistance contact with the soil has thus been obtained for the grounding system. As a result, a galvanic cell exists with lead anodic to copper. The lead sheath corrodes, protecting the copper grounds.

Polyethylene or neoprene jacketed cables should be used instead of bare lead sheath cables. Where bare or jute-coated lead sheath cables are installed, copper grounds should not be used; instead, use stainless steel, galvanized steel, stainless clad or similar rods, and apply cathodic protection. Cathodic protection will not be needed on jacketed cables if jackets remain intact. Taped splices, however, could be a problem.

4.15.13 Underground Tanks. Underground tanks frequently contain hazardous materials such as gasoline, butane, solvents and fuel oil. Unlike pipelines, which are usually repaired if a leak occurs, leaking tanks usually must be replaced. Consequently, corrosion exacts a large replacement cost plus the possibility of shutdowns. In addition, and frequently of major concern, a safety hazard is presented by leaking tank contents (paragraph 4.15.2).

Coatings and cathodic protection, applied to underground tanks, will not mitigate corrosion problems. Coatings alone are unsatisfactory. Corrosion concentrates at "holidays", increasing the corrosion rate ("area effect", paragraph 3.2.3.3.a).

Non-metallic tanks, notably fiberglass reinforced plastic, are being used commonly. These, along with non-metallic piping, often represent an economical solution to corrosion problems. They resist attack by many products, are strong enough to withstand most soil or other loading stresses, and are often not difficult to handle and install. They do, however, require some special procedures with which all contractors are not experienced. As with other underground structures, the engineer should select the best material for the job that is to be done.

Standardized cathodic protection systems - either galvanic or impressed current - are available for underground tanks. To insure adequate protection and proper operation, these require maintenance, and inspection by a qualified corrosion engineer.

4.15.14 Marine Structures. Sea water as an electrolyte is discussed in paragraph 3.2.3.2.c(2). Because it contains large amounts of dissolved salts, sea water is very conductive and, therefore, conducive to corrosion. In addition, it contains numerous organisms and dissolved

gases among other constituents. Variations in salinity and temperature can also contribute to corrosion. The effects of alternate wetting and drying, water velocity, and the mud line are also important.

When a new structure is being planned, the designer must consider corrosion control. Structure design should incorporate features to minimize corrosion. Among other factors, enclosed areas should be sealed to keep water out, skip welds should be avoided as should horizontal bracing in the splash zone.

A study should be made to determine what protective measures are needed. The corrosion engineer must consider structure life, corrosiveness of the water, and costs of corrosion control versus other means of maintenance such as repair or replacement.

There are many methods for controlling marine corrosion. Among the most important are: material selection, coatings, cathodic protection, concrete casing, and metal sheathing. Several examples indicate methods of analysis.

4.15.14.1 Existing Pier. This pier was a 22-year old structure, utilizing both H piles and sheet pile bulkheads in a sea water harbor. The water was slightly polluted, and its resistivity averaged 22 ohm-centimeters. No stray current was found. The piling had been coated with concrete in the tidal zone, and no corrosion had occurred there. In the water zone, however, H pile flanges had lost an average of about 0.265 inches, or 43% of original thickness. This is equivalent to 0.006 inches per year, quite close to the worldwide salt water corrosion rate for steel of 0.005 inches per year (reference 14).

Another 20 to 50 years of service was desired from this pier. Investigation revealed that protective measures would be required. To insure structural integrity, pile reinforcement was considered essential by the owner's engineers. Three means of reinforcement had been proposed. These were 1) welding in new pile sections between mud line and dock, 2) jacketing existing piles with concrete down to the mud line and 3) adding new "helper" piles adjacent to existing piles.

All three reinforcement alternatives required careful consideration. New pile sections would corrode faster than the existing piles because new sections would be anodic to old piles into which they were welded. Jacketing piles with concrete would lead to accelerated corrosion in mud due to the concrete-mud cell. Helper piles, if not electrically continuous with existing piles, would corrode at

about the same rate as the original piles. If helper piles were in contact with old piles, the helpers would corrode at an accelerated rate. Consequently, due to the desired 20 to 50 year service, pile reinforcement without corrosion protection would be only a partial solution. Additional repairs would likely be needed within the next 20 years.

Cathodic protection of the piles was determined to be the most desirable alternative. A design life of twenty years, using either impressed current or galvanic anodes, was most economical. Galvanic anodes would require replacement after 10 years. Economic analysis determined impressed current was the better choice. In addition, tidal zone coating and interpile bonds for electrical continuity were used.

4.15.14.2 Existing Docks. Twenty-year old docks supported by cylindrical steel piles were corroding severely. Land fill at the base of the piers was held by sheet steel piling. Piles and bracing on one pier were partially coated while the other structure was bare. Water was polluted and had a resistivity of 45 ohm-centimeters. No stray current was found.

Investigation revealed 35% of the piles had been reduced to about 50% of original wall thickness. About 2.5% of the piles had failed completely. The sheet pile bulkhead exhibited heavy scaling and about 85% of the tie rods had failed. Bracing was generally 50% corroded off at the ends.

In order to provide the extended service desired from the piers, corrosion protection was necessary. Severely corroded piles would need repairs, most probably by welding reinforcement pieces onto piles and bracing. Either a 20 or 50-year additional life was considered, so it was necessary to determine the best type of protection for the two life spans.

Four alternatives were: 1) cathodic protection with tidal zone and sheet piling coating, 2) coating only, 3) cathodic protection only and 4) no protection at all. Solution 1 was the best from a corrosion mitigation standpoint, since all surfaces would be protected. Solutions 2 and 3 offered only partial protection since corrosion in the water and mud would continue under Solution 2, and tidal zone corrosion would continue under Solution 3. For Solution 4, a program of regular pile repair would be required.

An economic analysis revealed that costs of the four alternatives were comparable. To insure structural integrity and minimize repair inconveniences, Solution 1) was chosen.

4.15.15 Underground Heat Distribution System Metallic Conduit. These systems consist of a carrier pipe or pipes,

often surrounded by thermal insulation encased in an exterior conduit. Metal, concrete and asbestos cement conduits are used. The carrier pipe is nearly always steel, although copper is sometimes found. Occasionally, steel and copper pipes have been used in the same conduit; this practice leads to serious galvanic corrosion of steel due to contact of dissimilar metals when the insulation becomes wet. Except in pressure-tight conduit which is protected against penetration (or non-metallic conduit) and thus assumed to remain dry, dissimilar metals should not be used.

Non-pressure tight conduits, which to our knowledge are no longer being made but many of which are still in use, present special problems. Water can enter conduit through joints or back up from flooded manholes. If insulation is present, this may become soaked, causing thermal as well as corrosion losses.

In conduit systems, the carrier pipe cannot be protected unless anodes are installed within the conduit. This is not standard practice. Therefore, it is necessary to keep water out of the conduit. This has led to development of pressure-tight conduits. It then becomes necessary to protect the exterior casing against corrosion.

When a leak occurs in the carrier pipe, water can flood the circuit and cause further corrosion. Leaks usually require replacement of a section of conduit since it is difficult to repair an individual leak unlike direct burial line.

In general, when steel conduits are used, coating and cathodic protection should be applied. Conduit manufacturers recommend this, too. In many environments, however, pressure-tight asbestos cement conduits should be considered. Some of these have the added advantage of having individually-sealed lengths. Thus, should a leak in one length occur, water would not flow to adjacent lengths, confining corrosion to the area of the leak.

It is important to remember that cathodic protection provides protective current to casing but not to enclosed piping. Cathodic protection is applied to buried conduit just as it is to pipelines, tanks, etc. The purpose is to protect the exterior conduit from corrosion; if corrosion is permitted to occur, then the exterior conduit will penetrate and admit water, leading to corrosion of the pipes within. Since the conduit acts as a shield, it is not possible to protect the carrier pipes from outside the conduit. Consequently, it is important to protect the conduit.

Some manufacturers and suppliers sell standardized galvanic anode systems along with their piping. These are not generally effective and should be tested by a competent engineer.

4.15.16 De-Icing Salts. De-icing salts are a problem in cold, Northern areas where snow and ice are abundant. Salts, spread on sidewalks, roads, etc. to melt ice, are extremely corrosive when dissolved in water. They get into manholes by being thrown there or by seeping in dissolved in melted ice. They can cause serious corrosion in ducts. This environment is similar in some respects to salt or brackish water encountered by seacoasts.

Dissolved salts also seep down through soil, attacking pipes, building piles, tanks and other underground structures. Salts have been found as deep as 5 to 6 feet below grade. Often, soil resistivity is greatly lowered by de-icing salts, increasing the corrosiveness. Where pipes are encased in concrete (snow melting and radiant heating systems), salty water can greatly increase corrosion at expansion joints or breaks.

4.15.17 Steam Condensate Lines. Steam condensate lines can fail from either internal or external corrosion. Most external problems occur on condensate or "return" lines since they are at a relatively high temperature below the boiling point of water and do not dry the environment about them as steam supply lines generally do. A recent study by the Academy of Science confirmed this (reference 13). Usually, these are surrounded by thermal insulation and encased in conduit (paragraph 4.15.15). Recently, however, condensate and return lines have been buried without any thermal insulation. This pipe behaves as any other buried pipe, and corrosion may cause failure. Where steel is used, coating and cathodic protection is needed. Coating must be compatible with line temperature. Generally, above about 160°F coal-tar epoxy is recommended (temperature limit, 250°F). Consideration should also be given to asbestos cement or other non-metallic pipe.

Interior corrosion also contributes to failures, and can occur in both supply and return lines. This is usually due to lack of or inadequate water treatment. The composition of metal or alloy (usually low carbon steel) used for piping generally is of minor importance. When interior corrosion is encountered, a study should be made to determine the cause and to select or modify treatment.

Problems encountered are of two types: plugging of lines with insoluble scale and deposits, or pitting and channeling of pipe walls. Deposits are generally metallic oxides and hydrates, and these are frequently found downstream from the location of corrosion. These deposits can be differentiated from material, not the result of corrosion, because of their metallic nature.

Pitting and channeling are produced by dissolved oxygen and carbon dioxide. Feed waters are generally saturated with dissolved oxygen from the atmosphere. Carbon dioxide may be present in various concentrations, derived from the atmosphere, or subterranean and other sources. In addition, carbon dioxide is liberated in water upon heating, from such compounds as calcium or magnesium bicarbonate.

Oxygen reacts with a metal surface as described in paragraph 4.3. Pitting and tubercles are commonly observed. Typical corrosion by carbon dioxide is uniform thinning of the surface, resulting in bright metal free from corrosion products. Control of this type internal corrosion can be accomplished by: boiler feed water treatment to minimize dissolved gases, chemical treatment of the condensate, or use of more resistant materials. Usually, the first two methods are less expensive. For information regarding water treatment, refer to Air Force Manual 85-12.

4.15.18 Other Internal Corrosion Problems. For a discussion on internal corrosion problems encountered in military facilities, see Air Force Manual 85-20 and other military directives applying to the specific structure under consideration.

4.15.19 Radio and Radar Tower Footings and Guy Anchors. Tower footings and guy anchors experience corrosion problems. These structures are usually galvanized steel, sometimes encased in concrete. Above-ground galvanizing generally provides adequate protection, but underground the cathodic protection it supplies to steel does not last long. Concrete casing may be included either as weight or to prevent contact with soil. As a coating, concrete is generally imperfect; corrosion concentrates at breaks.

Severe corrosion frequently occurs from the galvanic cell between steel tower footings or guy anchors and massive copper grounds. Often these structures are part of radio stations so they are tied to high power sources. Good grounding is therefore necessary. The large copper cathodes corrode the steel structures. This condition is worsened because towers are often located in areas of low resistivity (corrosive) soil to improve grounding. Other galvanic cells may occur when aluminum or copper are used in combination with steel in towers. Such dissimilar metals should be avoided where possible.

SECTION 5 - CORROSION CONTROL

5.1 GENERAL. The many reasons to initiate a corrosion control program for proposed or existing structures were discussed in Section 2. A few are:

- To insure continuity of operations for the success of the mission,

- To minimize hazards to life, limb, product or environment that a failure could cause,

- To satisfy government regulations,

- To minimize product or material losses,

- To minimize future expenditures resulting from structural deterioration, thus minimizing annual operating costs.

The relative importance of these, as well as the choice of specific corrosion control methods, depends on individual structure or system conditions. The situation should be analyzed by a competent corrosion engineer to determine types and rates of corrosion experienced or anticipated, and what means of control to use.

Corrosion should be considered from the preliminary planning stage to completion of all projects. Soils and waters are tested for resistivity, pH, and sulfate content so that underground facilities can be engineered for their environment. This is much more economical than the "trial-and-error" method of waiting until failures occur to investigate and correct premature deterioration. Mitigative measures most always cost less when installed on newly constructed facilities. They must, however, then be capitalized. Once underground structures have been operated, corrosion control costs often are included with operating or maintenance expenses. This may save money, or only appear to, until costs of plant shutdowns, excavations through floors, etc. are realized.

Corrosion control is often economically applied to existing buried piping, tanks, cables, and so on; even those which have suffered failures. This is an alternative to replacement, but its limitations must be understood (paragraph 5.2.2).

Corrosion may be prevented or mitigated readily, and all methods have one basic feature in common. That is, they reduce, stop or divert the flow of electric current which causes corrosion. This may be accomplished by physical, chemical or electrical means. Common methods of corrosion control include:

1. Material selection
2. Coatings and wrappers
3. Chemical treatment
4. Insulation
5. Bonding
6. Test stations
7. Cathodic protection
8. Anodic protection
9. Electrical grounding
10. Controlling the environment

These are often used in combination.

In order to decide what means of corrosion control to employ, it is often helpful to determine sources of corrosive current. For example, stray currents and galvanic couples can frequently be controlled more effectively when recognized. The difference between simple electrochemical corrosion and stray current corrosion as well as physical and chemical factors should also be considered.

5.1.1 Simple Electrochemical Corrosion. Galvanic and other types of electrochemical corrosion were discussed in Section 4. In general, these types are characterized by generation of corrosion current internally; that is, from conditions within the corrosion cell itself. The conditions produce a natural potential difference between anode and cathode. In order to mitigate electrochemical corrosion, contributing conditions within the corrosion cell must be recognized and altered or eliminated. Section 4 covers conditions which give rise to various types of corrosion. Methods of controlling corrosion are discussed in Section 5.

5.1.2 Stray Current Corrosion. As noted in paragraph 4.13, stray current corrosion is caused by current from some source external to the four components of a basic corrosion cell (paragraph 3.2.3). Although stray current corrosion is electrochemical in nature, it is generally considered separately from other electrochemical forms because of the external current source. Stray current corrosion is similar in nature to an electrolytic cell (paragraph 3.5.1). Whereas other forms of electrochemical corrosion correspond to galvanic or concentration cells (paragraphs 3.5.2-3).

Recognizing stray current corrosion usually requires an electrical analysis, somewhat different than for other corrosion. Mitigation is also usually different: eliminating the external current source or overcoming its effects by installing electrical equipment or rewiring the source, rather than altering the basic corrosion cell itself.

5.2 RECOMMENDATIONS FOR PROPOSED AND EXISTING STRUCTURES. It is generally easier to consider more possible means of control for a proposed structure, because less difficulty and expense is encountered than with a structure already in service. Early planning is more economical. With existing structures, however, anticipated problems may be more easily recognized because a history of in-service behavior is generally available.

5.2.1 Proposed Structures. Avoid bimetallic contacts.

Where different metals must be adjoining, insulate them to prevent contact or use those metals close in potential in the Galvanic Series. Coatings and cathodic protection are also effective in preventing galvanic corrosion. If coating alone is used, coat the cathode, not the anode; eliminate the "area effect" by preventing a small anode to cathode area ratio.

Choose materials of construction for environmental compatibility as well as other requirements.

Assure proper metal heat treatment or stress relieving if needed. Careful welding, to avoid "knife-line" attack, is essential.

Avoid crevices, corners, and other places where corrosives can collect.

Structures must be large enough to withstand required flow rates without experiencing cavitation or impingement.

Avoid designs including areas of turbulence; streamline bends.

Avoid spraying fluid onto metal surfaces.

Avoid conditions producing fluid stagnation.

Design for system environment temperatures.

Use inhibitors or chemical treatment where required in fluid environments.

Consider earlier experiences and/or experiences of others in the same area.

Excavated or removed structural members from the proposed site should be examined for corrosion.

Provide a uniform backfill for buried structures where possible.

Use soil tests and visual observation of soils as guides. Soil resistivity, pH, chemical content (sulfate, sulfide, chloride, etc.) and redox can be measured. Soil type, drainage and water table is observable.

Similar tests are run for water.

Avoid undesirable environmental conditions such as soil-concrete cells.

Study existing structures on the site or right-of-way. This may apply to plant expansion or pipeline looping projects. Here electrical measurements of structure-to-soil voltage, IR drop and structure-to-structure voltage can be taken. Nondestructive thickness measurements can also be considered. When some cathodic protection is already in use, the electrical evaluation might show that new facilities (especially if coated) can be cathodically protected at little or no additional cost. Stray current may be found. This might provide "free" cathodic protection when drained or entirely rule out cathodic protection.

Consider present and future conditions: Do not place metal structures under thick or inaccessible paved streets or floors. Avoid conditions where explosions, fires, or plant shutdowns may result from corrosion. Consider possible spilling or dumping of chemicals, deicing salts or other corrosives in the soil. Consider nearby future construction.

Require proper electrical grounding procedures.

Use coatings and cathodic protection where conditions warrant this. (Cathodic protection is generally less expensive when installed with the structure, rather than later.)

Install test stations where needed, whether or not cathodic protection is under consideration.

Use dielectric insulation and bonds where needed to prevent or help prevent corrosion.

Consider anodic protection where feasible.

5.2.2 Existing Structures. The same factors must be studied when considering existing structures. However, here a history is generally available. Failure rate and pitting experience can be analyzed to give a truer picture of past, present and future conditions. Also, structures can be tested with measurements of corrosion potentials and flowing currents showing actual conditions. These test data can be used to locate corroding areas and to correlate with actual experience for estimation of corrosion rates.

Corrosion failure expectancy curves are a valuable tool in the study of existing structures. Pipeline and cable systems should have records of their corrosion leaks. Each year's total is plotted cumulatively against time. If a logarithmic scale is used for the total failures to date, a linear time scale yields a straight line curve. This curve can be projected into the future. Figure 2-2 is an example, plotted for a large pipeline system.

Cathodic protection is often considered for an existing structure with a failure history. Here, replacement and/or extensive repair may be an alternate to cathodic protection. Dollar values are placed on corrosion failures, corrosion control costs are estimated and projected expectancy curves will show payouts. Figure 2-3 shows how various types of cathodic protection systems can be compared with corrosion leak repair. If replacement is determined to be the most economical choice, recommendations for proposed structures (paragraph 5.2.1) should be referred to.

When considering corrosion control for an existing structure, its future should be studied. If a pipe will be too small to handle the flow three years from this date, possibly all thoughts of corrosion control should be abandoned. On the other hand, if it is now a crude oil line and will next year be converted to LPG service, it is probable that every precaution should be taken. Changing environmental conditions must also be considered.

5.3 SELECTION OF MATERIALS. Engineering materials are frequently chosen for physical and mechanical requirements and initial cost only. Corrosion resistance may not be considered until after installation, if at all. This is not always the most economical approach, as was shown in Section 2. A material's corrosion properties must be considered also.

5.3.1 Factors Influencing Choice. Comparison of corrosion properties of various materials can be made only for a specific situation. The precise environment and application greatly influence how a material will react and must, therefore, be considered in any comparison.

5.3.1.1 Environment. Environmental factors that should be considered in material selection include composition, concentration, temperature, pressure, pH, velocity, turbulence, and homogeneity. cursory examination of the subject environment often indicates which factors are of prime importance.

a. **Atmospheres.** Deterioration of metals from atmospheric exposure is the most prevalent form of corrosion; for this reason, atmospheric corrosion receives more attention than some hidden forms of corrosion. To some extent, this

is justifiable; for example, it is estimated that at least 80 percent of the steel in use is subject to this type corrosion.

Controlling variables for atmospheric corrosion of a given metal are length of time the metal surface is wetted, types and amounts of foreign matter in the atmosphere in contact with the metal surface, temperature, relative humidity, precipitation, wind direction and velocity, and solar radiation.

Formerly, much confusion existed in corrosion detection of metals because some lasted longer at one test site than at another. Examples of centuries-old ferrous metal columns were used to indicate that better cast iron and steel were made in ancient times. Recent data have shown that such instances can merely reflect different atmospheric conditions in various parts of the world. Table 5-1 shows the difference in corrosion losses from tests at twenty worldwide locations. The table has been arranged by lowest to highest relative corrodibility.

Table 5-1

Relative Corrodibility of Atmospheres at
Twenty Locations Throughout the World¹

Location	Types of Atmosphere	Losses of Weight ² grams			Relative Corrodibility ³
		Max.	Min.	Mean	
Khartoum, Egypt	Dry inland	0.28	0.05	0.16	1
Abisco, North Sweden	Unpolluted	0.72	0.34	0.46	3
Aro, Nigeria	Tropical inland	1.53	0.74	1.19	8
Singapore, Malaya	Tropical marine	1.74	1.05	1.36	9
Basrah, Iran	Dry inland	2.17	0.68	1.39	9
Apapa, Nigeria	Tropical marine	2.94	1.47	2.29	15
State College, Pa.	Rural			3.75	25
South Bend, Pa.	Semirural			4.27	29
Berlin, Germany	Semi-industrial	4.83	4.55	4.71	32
Llanwrtyd Wells, B.I.	Semimarine	6.22	3.40	5.23	35
Kure Beach, N.C.	Marine			5.78	38
Calshot, B.I.	Marine	7.19	4.22	6.10	41
Sandy Hook, N.J.	Marine, semi-industrial			7.34	50
Congella, S. Africa	Marine	11.13	5.61	7.34	50
Kearney, N.J.	Industrial marine			7.75	52
Motherwell, B.I.	Industrial	9.39	6.57	8.17	55
Vandergrift, Pa.	Industrial			8.34	56
Pittsburgh, Pa.	Industrial			9.65	65
Sheffield, B.I.	Industrial	13.40	8.74	11.53	78
Frodingham, B.I.	Industrial	23.40	10.37	14.81	100

¹ Larrabee, C.P., "Corrosion of Steels in Marine Atmospheres and in Sea Water", Trans. Electrochem. Soc., 87, 1945. Based on field tests of the Iron and Steel Institute Corrosion Committee reported by J.C. Hudson (J. Iron Steel Inst., 11, 209, 1943), with additional data.

² Losses of weight sustained by 5.1- by 10.2- cm. (2- by 4- inc.) specimens made of open-hearth iron (0.007 percent copper) are used as a criterion (1.03 dm² of surface).

³ Frodingham, British Island = 100.

It is apparent from this table that atmospheric factors greatly influence corrosion properties. The most corrosive environments, marine and industrial atmospheres, are described here.

(1) Marine atmospheres. Sea air contains traces of chlorides and other components that, over time, can concentrate on metal surfaces. Also, salt spray is carried in the atmosphere around the sea coast. For example, during hurricanes, salt spray has been carried several hundred miles inland with resultant destructive effects on foliage. Usually, however, there is a very rapid drop-off in corrosivity with increasing distances from water. It has been found, for example, that corrosion samples exposed within 80 feet of water's edge deteriorated much more rapidly than those placed several hundred feet inland, say at 800 feet.

(2) Industrial atmospheres. Industrial atmospheres are among the most corrosive. These contain many pollutants, the most corrosive being sulfur compounds and chlorides. Sulfur dioxide from fossil fuel combustion combines with moisture in air or dew on surfaces to produce sulfurous acid. This compound is oxidized to sulfuric acid which beads on structure surfaces, producing severe acid conditions. Intense corrosion results. Various chloride compounds contribute to the intensely corrosive atmospheres, often producing worse destruction than sulfur acids.

b. Waters. Water containing no dissolved gases or other corrosive impurities does not react with metals to an appreciable extent. It also contains few ions to carry current and is a poor electrolyte. If oxygen is introduced into pure water, however, very corrosive conditions, typified by dimineralized water, result. This type water is more corrosive than fresh or salt water because it contains no carbonates. Carbonates often form protective films on metal surface.

Commonly encountered waters contain many contaminants. Their resistivities are lower, and, hence, they are better electrolytes. Also, carbon dioxide, sulfates, chlorides, and acids, compounds which can react with metals and other materials, are often present. Some or all of these contaminants can be found in sea water, waste effluents, and industrial waters from many sources. These waters can be extremely corrosive, their rate of attack usually increasing with temperature.

The most notable "contaminant" in water in terms of corrosion is oxygen, which dissolves from air. Oxygen, a cathodic depolarizer, reacts with protective films on metal cathodes. When the cathode film is gone, current flows, and corrosion proceeds.

Many other factors may increase corrosivity of waters. Suspended solids and entrained gas bubbles can contribute by impinging on structure surfaces, damaging coatings or protective films. Turbulence or high velocity flow may influence corrosion rates also. Analyses of individual water conditions are necessary to determine corrosivity.

c. Soils. Soil resistivity is one indicator of soil corrosivity. It is a measure of the ability of soil to permit electric current to flow and is expressed in ohm-centimeters. It is also used in cathodic protection design to predict current output from anodes. The lower soil resistivity, the more corrosive the soil may be. Soil with resistivities of less than 10,000 ohm-centimeters will cause significant corrosion to steel structures within a relatively short period; 20 years for 0.325 wall steel is one indication. The corrosive nature diminishes but is not eliminated at higher resistivities. Soil resistivity will vary during a given time period because of changes in moisture content. The most corrosive condition will be that with the highest moisture content. Extreme variations in resistivity throughout a site are also important.

Soil containing different materials, such as clay and sand, may have high average resistivity, but these materials have widely differing resistivities individually. Sand resistivities may vary from 5,000 to 100,000 ohm-centimeters and clay may vary from 200 to 10,000 ohm-centimeters. These differing resistivities represent different electrolytes and, when mixed, cause more rapid corrosion from dissimilar environments.

Soils with resistivities above 10,000 ohm-centimeters may be corrosive because of other environmental factors such as acidity or stray current.

The pH of most soils varies between 4 and 9. pH values below about 6 should be considered possibly corrosive due to acids in soils. In general, extremely high pH values and extremely low ones indicate a corrosive environment (other factors excluded). pH values around neutrality (approximately 6 to 8) are most favorable for growth of sulfate-reducing (anaerobic) bacteria.

De-icing salts are generally encountered in urban and suburban areas with appreciable snowfalls. The effect of de-icing salts is to lower soil resistivity in areas where used, by adding soluble salts to moisture in soils and acting as an improved electrical conductor. These salts accumulate every year in these areas and are carried farther from their source by dissolving in the ground water. Effects of de-icing salts have been reported down to depths of 5 to 6 feet. This presents an ever-increasing problem to underground metallic structures (paragraph 4.15.16).

Excavation of land can also cause soil corrosion, for several reasons. Excavated soil layers used as backfill are not replaced in their original order, and the degree of compaction will not be the same. Backfilling can mix soil types of widely-differing resistivities, setting up differential environment corrosion cells. Differential aeration cells can be set up by unequal compaction. Serious corrosion can occur because of sticks, stones, tin cans, welding rod, or other debris. Even though a clean, sand backfill is used, foreign materials may be inadvertently included in the backfill. Also, contaminated ground water can seep in, changing the environment of the backfill.

Foreign matter can also produce corrosive conditions in otherwise seemingly non-corrosive soils (favorable resistivity and pH). Cinders, for example, are a source of corrosion, especially where ferrous metals are concerned. Cinders contain appreciable amounts of sulfur, which, in aqueous media, forms sulfuric acid and aggressively attacks steel structures. Cinders are often contained in backfill materials and, while a buried tank is carefully backfilled with sand, aqueous solutions from surrounding soils will still seep into the cleanest sand backfill. A cinder, placed directly against bare metal, will make it impossible to cathodically protect that portion of the surface directly in contact with it.

Other problems arise, from impurities in soils which produce bacteria. Bacteria thrive where sewage or other organic material contaminates the ground. Leaky sewerage, septic systems, or outhouses, animal manure and other fertilizers also are a source. In addition, organic matter such as leaves, skids, rope and paper that are left in the ditch after construction provide a good environment for bacterial growth. Bacteriological corrosion was discussed in paragraph 4.4.

Soil surveys should always be made prior to design of new installations, to determine resistivity and extent and type impurities present in soil. However, these studies may not tell the complete story, and do not predict future environmental changes.

d. Other Environments. Many other environments besides the atmosphere, water, or soil contact common materials of construction. Natural gas, petroleum products, and chemicals are some which are commonly encountered. In any environment, an analysis of major constituents will help to determine materials resistant to degradation.

5.3.1.2 Application. In addition to knowledge of a material's proposed environment, the precise application should be analyzed prior to material selection. From such

an analysis, required properties can be determined; strength, ductility, thermal and electrical properties are common choices. Other factors that sometimes influence material selection include density, resistance to atomic radiation, and acoustical properties. These may be equally as important as corrosion resistance in some applications; consequently, a compromise which provides the optimum combination of properties and costs will be necessary.

Some materials, corrosion resistant in most circumstances, are subject to localized corrosion failures in certain applications. A material which is resistant to acidic corrosion may be used to fabricate a holding tank. However, if the same material is subject to high velocity corrosion, the stirring apparatus in this same tank may have to be formed of a totally different material. Consideration of all properties determines which material is best for any specific application.

In general, many potential problems can be avoided through proper design. Galvanic couples, crevices and pockets, and high stress conditions among others can often be avoided in the design stage.

5.3.2 Common Metals and Their Corrosion Properties. As stated earlier, a material's corrosion performance depends on many factors characteristic of specific conditions and application at hand. A general analysis of corrosion properties of metals commonly used for engineering is presented here.

5.3.2.1 Cast Iron. The term cast iron describes high carbon-iron alloys containing silicon and other elements.

a. **Gray Cast Iron.** Gray cast iron contains free flakes of graphite in the microstructure. Since graphite is very low in strength, its presence reduces the tensile properties of iron. Graphite also decreases ductility and makes gray cast iron susceptible to graphitization (paragraph 4.5). The material, however, is relatively inexpensive and easily cast at low temperatures. It also exhibits excellent vibration-damping capacity which recommends its use for such applications as heavy machine bases.

b. **Ductile (Nodular) Cast Iron.** Ductile cast iron contains free graphite as nodules or spheroids, a form less subject to stress concentrations than flakes. The result is increased ductility which allows some mechanical working of ductile iron. This form results from addition of magnesium or cerium to molten iron. As with any cast iron containing free graphite, ductile cast iron is subject to graphitization.

c. **Malleable Cast Iron.** "Clusters" of free graphite resulting from a heat treatment process characterize malleable cast iron. This material shows good ductility.

d. White Cast Iron. If the amount of silicon in cast iron is reduced below about 1%, practically all carbon present forms carbides. With no graphite in the microstructure, graphitization will not occur. However, the high carbide content of white cast iron produces a metal which is very brittle and quite hard.

e. High Silicon Cast Iron. Gray cast iron containing silicon in excess of 14% is extremely corrosion resistant, due to a surface layer of inert silicon dioxide. Hydrofluoric acid is one of few corrosives which can attack this alloy. When chromium is added, resistance increases further. High silicon cast irons are corrosion resistant to the entire range of sulfuric acid concentrations up to the boiling point, to strong nitric acid, and to many hydrochloric acid conditions - often to high temperatures, and to most other mineral and organic acids. These materials have fair tensile strength and are not ductile. They are susceptible to thermal and mechanical shock. The hardness of such alloys makes them resistant to many conditions involving severe corrosion-erosions. The alloy is subject to chipping. High-silicon, chromium-bearing cast iron is used extensively for anodes in impressed current cathodic protection systems.

f. Austenitic Cast Irons. Austenitic gray cast iron alloys contain 20 percent nickel or nickel and copper in the ratio 2.5 to 1. They represent most common types of the austenitic cast irons. Such special irons are more highly resistant to chemical attack and less active in galvanic action with graphite than are regular gray cast irons. These properties make them resistant to graphitization. The coefficients of thermal expansion are considerably less than those of normal gray cast irons. Austenitic gray cast iron alloys can be used to 1500°F as compared to 1200°F for gray iron, where only small permanent changes in dimensions may be tolerated.

These alloys are used in making valves, fittings, pumps, fatty acid stills, still-tube supports in the petroleum industry, gas-producing shells, sulfite digester blowpipes, salt filters, and containers that hold caustic solutions, crude oils, sulfuric acids, and refined petroleum products.

5.3.2.2 Carbon Steels. Plain carbon steels exhibit corrosion resistance similar to gray cast iron with an important exception. Carbon in carbon steel forms carbides, not graphite, and, therefore, graphitization of carbon steel is not a problem. This material is relatively inexpensive and finds many applications where good corrosion resistance is not a requirement.

5.3.2.3 Low Alloy Steels. Low alloy steels are carbon steel alloyed to elements in the range of about 2% total or less. Additions in small amount of such materials as chromium, nickel, copper, molybdenum, or vanadium fall into this

category. These materials are added in general to increase mechanical properties, not corrosion resistance, but some increase in resistance to corrosive attack is generally observed. Additions of small amounts - about 2% total or less - often appreciably increase resistance to atmospheric corrosion. Such alloys as 2% chrome - 1/2% molybdenum find extensive use for boiler superheater tubing, because of combined heat- and corrosion-resistance. However, low alloy steels with higher percentage additions are often susceptible to stress corrosion cracking, even under mild conditions.

5.3.2.4 Stainless Steels. Stainless steels exhibit higher corrosion resistance than other steels, because large amounts of chromium are added. Additions of from 10 to 30% make this material the main alloying element in the stainless group, although nickel, molybdenum, titanium, columbium, or copper are often added. Chromium is normally reactive but passivates in many environments. Alloys of chromium exhibit characteristic passivity. This is why stainless steel is corrosion resistant.

Since over 60 types of stainless steel exist, properties vary widely. Some are designed for high strength, some for machinability. The best known stainless steel is type 302. This is basic 18-8 steel (18 percent chromium and 8 percent nickel). Type 304 is much like 302, with lower limits on carbon content and higher mean chromium and nickel content. Type 316 is of the same family, with molybdenum added to increase corrosion resistance and high temperature strength. It can be used for many chemical tasks. Type 410 is a hardenable heat-resistant alloy with good machining properties. Types 201 and 202 have corrosion resistance comparable to 302, but contain less nickel and more manganese. The 20-alloy, highly alloyed stainless steel composition, augments conventional 18 percent chromium, 8 percent nickel stainless steel (ACI graded CF-8, CF-8M, and AISI types 304, 316) for more severe services, particularly for sulfuric acid use. It corresponds to ACI grade CN-7M and is available either cast or wrought. Coldworking is the only means of increasing the hardness of type 20-alloy. It finds extensive use for equipment as pumps, valves and agitators. The 20-alloy is superior to 18-8 alloys for other uses, such as contact with hot acetic acid, brines, strong, hot caustic solutions, hydrofluoric and hydrofluosilicic acids, hot sulfates and sulfites, sulfurous acid, phosphoric acid, and plating solutions. Sulfate solutions usually have enough free acidity to damage 18-8 alloys, and they require the superior composition of the 20-alloy.

In environments that are favorable to corrosion by oxidation, stainless steels display a nobility approaching that

of silver or platinum. When placed in strongly reducing media and deprived of oxygen, such alloys may move up the galvanic series to a vulnerable position approaching carbon steel.

Austenitic stainless steels - including all the most common ones - are subject to damaging carbide precipitation during welding operations. The explanation accepted for this phenomenon is the "chromium depletion theory". This theory suggested that under certain conditions (slow cooling or being held at about 1200°F for some time) chromium in the microstructure combines with carbon from steel to form chromium carbide. This compound generally precipitates at the grain boundaries, robbing this area of its protective dissolved chromium. Intergranular corrosion results. During welding, often regions slightly to either side of the weld are held at about 1200°F for a time, due to heat conduction through the metal. All coatings should be quench-annealed from 2000 to 2100°F after welding, to reduce possible intergranular corrosion.

Table 5-2 lists common applications of various stainless steels.

Table 5-2

STAINLESS STEEL APPLICATIONS

<u>Type</u>	<u>Equipment</u>
301	Chutes for abrasive solids
302	Heat exchangers, towers, tanks, pipe
302B	Heaters, heat exchangers
303	Pumps, valves, instruments, fittings
304	Perforated blowpit screens, heat-exchanger tubing, preheater tubes
305	Funnels, utensils, circular hoods
308	Welding rod; more ductile welds for Type 430
309	Welding rod for Type 304
310	Jacketed, high-temperature, high-pressure reactors, oil-refinery still tubes
316	Distillation and fractionating equipment for producing fatty acids, sulfite paper processing equipment, and fractionating towers, brine and sea water applications
317	Process equipment involving strong acids or chlorinated solvents
321	Furnace parts in presence of corrosive fumes
347	Like 302, but where carbide precipitation during fabricating or service may be harmful
403	Steam-turbine blades
405	Tower linings, baffles, separator towers
410	Bubble-tower parts for petroleum refining, coal-handling equipment, seal plates, roller trains of hydraulic gates, etc.
414	Beater bars, valve seats
416	Valve stems, plugs, gates, nuts, bolts
420	High-spring-temper applications, surgical equipment
430	Nitric acid storage tanks, furnace parts, fan scrolls
430F	Pump shafts, instrument parts, valve parts
431	Products requiring high yield point, resistance to shock
440A	Cutting edges, shear blades, ball bearings
440B	Cutting edges, shear blades
440C	Cutting edges, shear blades
446	Burner baffles, furnace linings

5.3.2.5 Aluminum and Alloys. Aluminum, passive to many environments, is used extensively for pipes, tubing, food containers, and kitchen utensils. It is extensively used in chemical and petroleum industries. In building construction, aluminum is used for roofing, window frames, and hardware. It is also used in aviation construction, machinery, electrical appliances, and as a metal paint. Aluminum should not be placed in continuous contact with soils or concrete. Resistance to weathering results from protective action of the superficial film of oxide (Al_2O_3) or hydrated oxide ($\text{Al}(\text{OH})_3$) that forms, tending to prevent further corrosion. This film can be artificially induced by anodizing, passing electric current through the metal surface.

Aluminum is amphoteric, that is, it reacts with either acids or alkalis. The oxide film protecting the metal is stable over an approximate pH range of 4.5 to 8.5. This can be altered by certain ions whose influence affects the film's resistance. Aluminum should not be used in acid or alkaline environment. Corrosion problems can arise if aluminum is in contact with concrete, an alkaline environment, unless concrete is kept bone dry. Aluminum is subject to pitting, crevice corrosion, stress corrosion, and exfoliation.

Aluminum alloys are inexpensive and strong, finding application where high thermal conductivity is required. Strength of aluminum alloys may be improved by alloying and heat treatment. Strengthening, however, tends to decrease corrosion resistance of these materials. One means of overcoming this effect is a process called cladding, covering the alloy surface with a thin skin of purer metal. Clad alloys resist pitting and stress corrosion, the cladding acting as an anode and protecting the base metal.

An important working alloy without heat-treatment properties is the 3003 alloy (formerly designated as 3S) which contains 1.25 percent manganese. It is resistant to heat and corrosion. Another important aluminum alloy is duraluminum, originally developed in Germany. In the United States, a similar alloy was developed, designated as 2017 alloy. This alloy is composed of 94 percent aluminum, 4 percent copper and 0.5 to 1 percent each of magnesium and manganese. It is heat-treated to 530°C or 986°F and then rapidly cooled by quenching in water. For about forty-five minutes, it is then in a plastic condition and can be rolled, bent, or worked cold. Many other aluminum alloys have been developed. Composition and available forms of aluminum alloys are given in Table 5-3 and applications are given in Table 5-4.

Table 5-3

AVAILABLE ALUMINUM ALLOYS AND THEIR COMPOSITION

<u>Type</u>	<u>Alloying Elements percent</u>		<u>Available Forms</u>
3003	Mn, 1.30	Cu, 0.20	Plate, sheet, wire, rod, extruded shapes, drawn tube and pipe, forgings
Clad 3003	Mn, 1.25 ¹	Cu, 0.20	Plate, sheet, drawn tube, and pipe
3004	Mn, 1.20	Mg, 1.00	Plate, sheet, drawn tube, and pipe
Clad 3004	Mn, 1.20	Mg, 1.00 ¹	Plate, sheet
5052	Mg, 2.50	Cr, 0.25	Plate, sheet, wire, rod, bar, drawn tube, and pipe
6053	Si, 0.70	Mg, 1.30	Rivets
	Cr, 0.25		
6061	Cu, 0.25	Si, 0.60	Plate, sheet, wire, rod, bar, rolled shapes, extruded shapes, drawn tube, and pipe
	Mg, 1.00		
	Cr, 0.25		
6063	Si, 0.40	Mg, 0.70	Extruded shapes, drawn tube, and pipe
43	Si, 5.00		Castings
355	Cu, 1.30	Si, 5.00	Castings
	Mg, 0.50		
356	Si, 7.00	Mg, 0.30	Castings
2017	Cu, 4.00	Mn, 0.50	Wire, rod, bar
	Mg, 0.50		
1100	Commercially pure aluminum		Plate, sheet, wire, rod, bar, rivets, forgings, forging stock, impact extrusions

¹ Properties of Clad 3003 and Clad 3004 are substantially the same as 3003 and 3004, respectively.

Table 5-4

Aluminum Alloy Applications ¹

Siding and roofing
Gutters and downspouts
Building facades
Door and window frames
Aircraft skin
Ventilation ducts
Heat exchangers
Boats and ships
Water-storage tanks
Cooking utensils
Canning equipment and cans
Piping
Underground chemicals
Above- and on-grade storage tanks
Reinforcing for fiber glass
Electrical conductors and cables
Transmission towers
Shielding inside communication cables
Lamp poles

¹ Also used extensively in chemical, rubber, soap, brewery, dairy, food, explosive, and paint industries, and for various electrical applications.

5.3.2.6 Copper and Alloys. Copper is an excellent material for many applications because it is relatively noble in many environments, it exhibits good electrical and thermal conductivity, and it is easily formable and strong. Because hydrogen evolution does not play a role in most corrosion of copper, this metal is resistant to attack by acids. However, if oxidizing agents are present, corrosion will occur. Copper is subject to stress corrosion in alkaline environments. Copper is often used for pipes and containers for corrosive solutions, and for tubing for gas, oil, and water. Copper ground rods are used extensively in utilities services. Roofing, gutters, waterspouts, water piping, air conditioning, store fronts, and screens made of copper are permanent as well as pleasing in appearance. Perhaps the most obvious use of copper is for electrical cable and conductors, because of its good electrical conductivity.

Copper alloys have inherently good resistance to corrosion. They are used widely in chemical processing particularly when heat and electrical conductivity are required. They often form films of insoluble corrosion products, which effectively protect the base metal. In some cases, an alloy that is highly resistant in stagnant solution may be attacked

by turbulent solution. Oxygen or oxidizing agents generally accelerate corrosion of copper alloys. Composition of copper alloys is given in Table 5-5 and applications in Table 5-6.

Copper alloys are resistant to most organic solvents such as acetates, alcohols, aldehydes, ketones, petroleum solvents, and others. Organic acids in aqueous solution may contact most copper alloys, but corrosion is not accelerated when air is present. Special brasses and brasses containing a minimum of 85 percent copper are moderately resistant to nonoxidizing acids.

Copper alloys are also resistant to attack by pure steam. Steam containing carbon dioxide, oxygen, and ammonia is not corrosive but condensate containing these elements is corrosive, particularly to brasses that are high in zinc content.

Often copper exhibits corrosion resistance at least partially because of cathodic protection received from other metals it contacts. This is especially common with ferrous metals, resulting in a galvanic cell with iron or steel corroding to protect copper. In such cases, copper actually corrodes the other metal. It may be necessary to coat the copper to lessen this problem, especially when the copper area is large relative to the anodic ferrous metal (area effect).

Another problem encountered with copper is corrosion of buried tubing (utility service lines, etc.) by deicing salts and fertilizers in soil (paragraph 4.15.1.1).

Copper and brasses are subject to cavitation and impingement corrosion. Above a critical water velocity of about 4 to 5 feet per second, copper water tubing may fail easily from this problem.

Binary copper-zinc alloys with less than 85 percent copper may be rapidly attacked by dezincification. Moist carbon dioxide is corrosive to brasses high in zinc; in contact with other copper alloys, however, it is generally noncorrosive. Moist chlorine gas and ammonia are corrosive to all copper alloys. Unless chloride hydrocarbons, such as carbon tetrachloride and trichloroethylene, are stabilized to assure neutrality, they are somewhat corrosive to copper alloys at the boiling point and in the presence of moisture. Alloys with more than 65 percent copper should not be used with wet gas under pressure. Sulfides are more corrosive to alloys high in copper than to brasses such as yellow brass, Muntz metal, Admiralty, or Tobin bronze. Copper alloys should not be used with oxidizing acids.

Table 5-5

Composition of Common Copper Alloys

<u>Alloy</u>	<u>Composition, percent</u>			
Brass, aluminum	Cu,76	Zn,21.96	Al,2	As,0.04
Brass, naval	Cu,60	Zn,39.25	Sn,0.75	
Brass, red	Cu,85	Zn,15		
Brass (arsenical admiralty)	Cu,70	Zn,28.96	Sn,1	As,0.04
Brass (Muntz metal)	Cu,60	Zn,40		
Bronze, aluminum	Cu,95	Al,5		
Bronze,phosphor	Cu,95.75	Sn,4	P,0.25	
Copper, Silicon	Cu,95.8	Si,3.1	Mn,1.1	
Cupro-nickel	Cu,80	Ni,20		

Table 5-6

Applications of Copper Alloys

<u>Industry</u>	<u>Equipment</u>	<u>Metals Used</u>
Brewing	Piping	Copper, red brass
Distilling	Piping	Copper, red brass
	Condensers	Copper, arsenical admiralty
	Gas cooler tubes	Arsenical admiralty
Oil refining	Condenser and heat-exchanger tubes	Arsenical admiralty, cupro-nickel, aluminum brass, red brass
	Tube sheets	Muntz metal, naval brass, cupro-nickel, aluminum bronze
Pulp and paper	Water piping	Copper, red brass
	Stock lines	Copper, copper-silicon
	Wire-Fourdrinier screens	Brass, phosphor bronze
	Slotted screen plates	Phosphor bronze, aluminum brass
Salt	Tubes for vacuum pans	Copper, arsenical admiralty, cupro-nickel
Sugar	Evaporator tubes	Copper, red brass, arsenical admiralty
	Calandrias, syrup tanks, mixers	Copper-silicon
	Heat exchanger tubes	Arsenical admiralty
	Tube sheets	Naval brass

5.3.2.7 Magnesium and Alloys. Magnesium finds application mainly because it is extremely lightweight but strong when alloyed. Magnesium is also anodic to most metals and therefore subject to galvanic corrosion. Impurities in the metal (such as iron, copper or nickel) serve as cathodes causing magnesium to corrode. Addition of small amounts of manganese, zinc and aluminum tend to offset some harm caused by these impurities.

Magnesium forms a protective oxide film in atmosphere. This supplies good corrosion resistance where salt is not present. Alloys are susceptible to erosion corrosion, pitting and stress corrosion, and are attacked by most acids. Magnesium is resistant to hydrofluoric acid, however, due to a protective layer of corrosion product which forms.

Magnesium is utilized in aircraft and aerospace applications, luggage, and portable equipment because of its light weight. This metal also finds application because of its anodic properties as galvanic anodes for cathodic protection (Section 7) and in batteries. Magnesium as galvanic soil anodes requires low-resistance backfill to obtain higher current output. These anodes will generally work in most soils even if not backfilled. However, backfilling assures more even and higher current output. Unalloyed magnesium is never used for anode materials. Various alloys are available for this purpose, depending on specific properties required of the anode.

5.3.2.8 Lead and Alloys. Lead is passive to many environments, particularly acids. It is used extensively for cable sheaths, pipes, and lining tanks and vessels for corrosive solutions. Lead and its alloys are widely used in cladding equipment for production, transmission, transportation, and storage of a variety of corrosive chemicals.

Corrosion resistance of lead and its alloys stems from a thin coating that forms on its surface. If the coating is one of highly-insoluble salts, such as the sulfate, carbonate, or phosphate, resistance to corrosion is high and the environment generally promotes self-healing when mechanical injury occurs to the film. Conversely, when a soluble film such as nitrate, acetate, or chloride forms, little protection is afforded, and the lead may corrode further. Likewise, if insoluble protective coatings are removed mechanically, for example, by abrasion or erosion, or if dissolved chemically, as in some forms of mixed corrosion, corrosion resistance is similarly reduced.

Chemical lead, acid lead, and copper lead are usually specified for chemical construction. Small amounts of silver and copper in such leads add to corrosion resistance of lead and improve creep and fatigue resistance.

Lead alloys with about 1 percent antimony and a small amount of tin have been used on electric power cables and telephone cables as sheath. Lead-antimony alloy of about 4 percent antimony is used as cladding for steel straps. Antimony adds strength to lead, but the strength greatly decreases with temperature. Lead cable sheaths are used either bare or coated, commonly with coal tar compounds and jute wrapper. They are frequently grounded or shielded from external noise and physical damage with copper, steel, or combinations of these. Such shielding or grounding may present problems with galvanic corrosion. Lead cables may be direct burial (buried) or placed in ducts (underground). Cathodic protection can be effective to mitigate corrosion of lead, but care must be taken to avoid excess current. Lead is amphoteric, and high current gives rise to alkaline conditions which are therefore corrosive. Stray current corrosion can be a serious problem with lead because the metal corrodes at a rate of about 75 pounds per ampere year (compared to 20 pounds per ampere year for ferrous metals).

5.3.2.9 Zinc and Alloys. Prime uses for zinc in corrosion control are as sacrificial coatings (galvanizing), galvanic anodes for cathodic protection, and as pigments to corrosion resistant paints. Zinc itself is not corrosion resistant. If the metal or its alloys are used in other applications, it is generally because of low-melting points for die casting; however, these castings are then usually coated with more-resistant metal.

Zinc readily passivates in soil or water containing carbonates, so use of a backfill is required for zinc anodes. It is also important to test the proposed environment for carbonates prior to use, as it may be impossible to use zinc at all.

5.3.2.10 Nickel and Alloys. Nickel and its alloys are prime engineering materials because of corrosion resistance, high strength and hardness properties, and ductility over a wide temperature range. Nickel imparts stress corrosion resistance to its alloys, and nickel alloys are highly resistant to alkaline solutions. Nickel and its alloys are attacked by strong oxidizing agents and sulfur-bearing, hot gases. Important alloys are discussed individually.

a. **Chlorimets.** Chlorimets contain about 60 percent nickel, plus chromium and molybdenum in major concentrations. They are extremely corrosion resistant and used for such applications as sulfuric acid solutions. The cost factor can be limiting, but they are used frequently nonetheless.

b. **Hastelloys.** Hastelloys are used under extreme corrosive conditions. They are expensive, yet economical in many situations encountered in the chemical process industry. High temperature properties are good. Composition and

applications of Hastelloys B, C, and D are given in Table 5-7.

Hastelloy B is nickel-molybdenum-iron alloy developed to resist certain severe corrosive conditions. It has good high temperature properties and is particularly well-suited for equipment that comes in contact with hydrochloric acid at all concentrations and temperatures and hydrogen chloride gas. It also has good corrosion resistance to sulfuric and phosphoric acids. Strong oxidizing agents should be avoided. Hastelloy B is similar to austenitic stainless steel in its working properties and microstructure. Full annealing of a fabricated vessel is recommended prior to service in severely corrosive environments.

Hastelloy C has excellent resistance to a wide variety of corrosives. It retains, to a large extent, the resistance of nickel-molybdenum alloys to nonoxidizing agents, whereas chromium provides general resistance to oxidizing agents. Hastelloy C is machinable and can be fabricated by most methods. It has high room temperature ductility and good weldability. To assure optimum corrosion resistance, finished units should be fully annealed to relieve stresses and dissolve all constituents except primary carbides. Annealing should be followed by rapid quenching in water or cooling in air. Hastelloy C is widely used when extremely hot strength is the primary requirement, as well as when high temperatures are combined with corrosive conditions.

Hastelloy D is most widely known for exceptional resistance to sulfuric acids of all concentrations and temperatures even up to the boiling point. The alloy also has good resistance to other corrosives, including phosphoric acid, organic acids and acid salts. It has high strength, good resistance to thermal shock, good abrasion resistance, and is somewhat difficult to machine. It is available only in cast form.

Table 5-7

Composition and Application of Hastelloys

<u>Hastelloy</u>	<u>Composition - percent</u>		<u>Application</u>
C	Mo, 16-18	Cr, 15.5-17.5	Heat exchangers for cooling aluminum chloride, hydrochloric acid streams with sea water. Valves, piping, and vessels for handling chlorine gas, wet and dry.
	Fe, 4.5-7	W, 3.75-4.75	
	C, 0.15 max.	Mn, 1.0 max.	
	Si, 1.0 max.	P, 0.04 max.	
	Ni, balance		
B	Mo, 26-30	Cr, 1.0 max.	Equipment for alkylation of benzene to ethyl benzene. Lining for isomerization towers in production of aviation gasoline.
	Fe, 4-7	C, 0.12 max.	
	Mn, 1.0 max.	Si, 1.0 max.	
	Ni, balance		
D	Cr, 1.0 max.	Fe, 1.0 max.	Heating tubes in Simonson-Mantius sulfuric acid concentrators and chemico-type concentrators. Check valves for handling yield from corrosive and sandy oil wells. Pumps handling sludge containing sulfuric acid.
	C, 0.12 max.	Mn, 0.80-1.25	
	Si, 8.50-10.0	Cu, 3.85-4.25	
	Ni, balance		

c. Monel. Monel is probably the most important copper-nickel alloy. It contains 67 percent nickel, 30 percent copper and is stronger than nickel. It is more resistant than nickel under reducing conditions and more resistant than copper under oxidizing conditions. Applications of Monel are given in Table 5-8.

Corrosion of Monel is practically nil in all concentrations of air-free sulfuric acid up to about 80 percent. Even in air-saturated acid below 80 percent, maximum corrosion is only 0.04 inch per year. Monel is second only to silver in resistance to hydrofluoric acid. Its use is not recommended, however, with oxidizing acids. Monel is available in casting, forgings, hot rolled bars, and sheets.

Table 5-8

Applications of Monel

<u>Application</u>	<u>Materials and Processes</u>
Equipment	Salts, by-product coke and gas industry, organic chlorinations, sugar manufacture, plastics, oil sulfonation, and rubber synthesis
Distillation	Fatty acids
Evaporators	Black liquor (tubes), zinc chloride (coils, tubes), aluminum sulfate
Fans, similar uses	Phosphoric acid (by phosphorus vaporization)
Gas filters	Ammonia oxidation
Preheaters, regenerators, strippers	Manufacture of avgas by HF alkylation
Screening, treatment, washing, handling	Pulp stocks
Turbine blades, valve trim, plates	Steam service (700°F to 800°F)
Valve trim, orifice plates	Chlorine service

d. Inconel. Inconel is an alloy that has the following composition: Ni, 77 percent; Cu, 0.2 percent; Fe, 7 percent; Cr, 15 percent; Si, 0.25 percent; Mn, 0.25 percent; C, 0.6 percent; and S, 0.007 percent. Inconel retains considerable resistance under reducing conditions. In strong oxidizing solutions it is practically free from attack because of the tendency of chromium to become passive by covering itself with a protective layer of oxide. When heated in air, the alloy resists progressive oxidation to about 2000°F. Such outstanding resistance to oxidation is supplemented by excellent creep characteristics. Applications of Inconel are given in Table 5-9.

Table 5-9

Inconel Applications

<u>Type of Application</u>	<u>Materials Being Handled</u>
Evaporators	Concentration of magnesium chloride (tubes)
Fermentation tanks	Processing of penicillin chloromycetin
Heaters	Sulfate digester liquor
Lined towers	Fat-splitting by continuous high-pressure high-temperature hydrolysis

5.3.2.11 Tin and Alloys. Tin's major use is as a protective coating for steel in "tin cans" containing food products. Normally cathodic to steel, in this application, potentials reverse, and tin becomes a sacrificial coating. Tin is a weak metal, soft and easily formed. Tin is somewhat resistant to atmospheric corrosion and is not attacked by distilled waters.

Tin is used for cans in paint, beverage, and petroleum industries as well as for food products. This metal is also used for handling distilled water, for medicants, and in solder. Tin foil is more expensive than aluminum foil and has been replaced by the latter for most applications.

5.3.2.12 Other Metals.

a. Titanium and Titanium Alloys. Titanium alloys are used for high corrosion resistance and high strength-to-weight ratio at temperatures up to 800°F. Titanium is immune to salt air and salt-water corrosion. It can be heated up to 1000°F, without impairing its properties by oxygen penetration. At elevated temperatures, it will react with fluorine, chlorine and iodine. It also reduces all known oxides. The iodine reaction is reversible, permitting production of

high-purity metal by dissociation of titanium iodide on a hot filament. Hydrogen chloride reacts at high temperatures to form titanium tetrachloride.

Improved manufacturing techniques and lowered costs are making titanium more competitive.

b. Tantalum. Tantalum is a high-priced metal which can be used in thin sheets to reduce costs. It resembles glass in chemical properties, and often is used to repair glass-lined equipment. This metal is highly corrosion resistant in most environments. It is attacked by alkaline solutions, and hydrofluoric acid and is subject to hydrogen embrittlement. Tantalum is used mainly in heat-transfer equipment.

c. Zirconium. Zirconium is resistant to most acids and alkalis. Practically inert at temperatures up to 390° F, it can be used at temperatures as high as 4000°F under oxidizing conditions. Impurities such as aluminum, carbon, and nitrogen impair corrosion resistance. Zirconium is subject to hydrogen embrittlement and rapid attack in high temperature waters. Zirconium is used for crucibles and tubes, plates, and other shapes, and in hydrochloric acid handling.

d. Columbium. Columbium is corrosion resistant to many environments at ordinary temperatures; corrosion rate is increased greatly at temperatures above 210°F. When added in small amounts to chrome steel, columbium will prevent intergranular corrosion. The amount of columbium required to prevent completely the intergranular attack should be about ten times the carbon content of steel.

e. Cadmium. Cadmium finds application mainly as an electroplated coating. Cadmium imparts resistance to corrosion fatigue to high-strength steels; this is important in aircraft. Cadmium is generally less effective than zinc as a sacrificial coating, and more expensive.

f. Noble Metals. Gold, platinum, and silver have excellent corrosion resistance but are prohibitively expensive. They are, however, used in industry and, of course, for jewelry. Often noble metals provide coatings for less expensive, stronger metals.

Gold is sometimes used in subminiature electronic assemblies where a buildup of corrosion product would affect the precise size and electrical behavior of the part. This metal is attacked by strong oxidizing agents such as aqua regia, and by chlorine, bromine, and mercury.

Platinum is frequently used as an anode, sometimes as a surface layer on titanium or tantalum. Platinized platinum makes a good auxiliary electrode for laboratory measurements requiring reproducibility. It is attacked by aqua regia, chlorine, bromine, and ferric chlorides.

Silver is used in electrical work where even slight corrosion of other metals would cause problems. Silver oxide, unlike the oxides of most metals, including copper, conducts electricity. Consequently, silver, corroded slightly, is still electrically sound and is dependable for rugged service like switches. Silver is attacked by strong acids and mercury and it will "tarnish" in air containing sulfur compounds.

5.3.3 Non-Metals.

5.3.3.1 Materials. Materials other than metals are used in corrosive environments. In many instances, strength and corrosion resistance are superior to metals, and the costs may be less.

a. Plastics. Plastics have become important materials of construction. The specific use of a plastic depends on its chemical, physical, and electrical properties. Plastics are used extensively in the chemical industry for handling corrosive liquids. Tanks, vats, kettles, pipes, and pump parts made of plastics are examples of their application in contact with corrosive environments. To cite an example of their application to insulation, plastics are used extensively as cable jackets. Some jackets are applied over lead-sheath cables to protect lead from corrosion. Lead-sheath in this case is used to exclude moisture, and plastic is used to isolate the lead-sheath from a corrosive environment.

Plastic is defined as a synthetic organic solid material whose chief component is a resinous binder. At some stage in its production, the binder is either plastic (capable of being shaped or extruded) or liquid (capable of being cast or otherwise made into the solid material) and, at some subsequent stage, it assumes a more or less rigid condition. Most plastics are produced synthetically, because they do not occur naturally. Processes such as condensation and polymerization yield plastics for practical usage.

Plastics are generally softer and weaker than metals. They have a lower temperature range and are easily melted. They are more resistant than most metals to substances such as chlorides but less resistant to solvents and oxidizing acids. Plastics do not corrode electrochemically like metals. Instead, they deteriorate and change properties by growing soft or hard, losing strength, or spalling and discoloring. Properties of plastics can be altered desirably with fillers, plasticizers, and hardeners.

Methods of fabrication used for plastics include casting, extrusion, calendaring, molding, and lamination. Laminated plastics are usually made from sheets of paper, cloth, or

wood impregnated with suitable resin, usually a phenolic, urea, or polyester type. Sheets are piled on one another to give the required thickness and then heated and pressed together.

Plastics are divided into thermosets (thermally reacting chemically to produce their final state), and thermoplastics (softened by heat but not depolymerizing on heating). Currently, thermoplastics are enjoying the greatest popularity in industrial and utilities applications.

(1) Thermoplastics. Thermoplastics are characterized by their ability to be reworked; they soften at increased temperatures and regain hardness upon cooling. Primary thermoplastics, employed as engineering materials, are described here.

(a) Polyethylene. Polyethylene currently makes up the greatest tonnage of all plastics produced. This plastic has excellent resistance to moisture. At ordinary temperatures, it has good resistance to both chemical and solvents and also to heat. By incorporating suitable pigments, it is resistant to ultraviolet light. High-molecular weight polyethylenes are fungi-resistant and have good electrical properties. At elevated temperatures, polyethylene is subject to thermal oxidation and, when exposed to light, it is subject to photo-oxidation. It is also subject to radial stress cracking. Two common types of derivatives of polyethylene are chlorosulfonated polyethylene and polymonochlorotrifluoroethylene. The derivatives are similar to polyethylene except that they are more polar; therefore, they have superior adherence and heat resistance.

Polyethylene has a wide variety of uses. It is commonly used for piping water and many chemicals. This plastic also is marketed for many household uses; ice trays and containers of all kinds are common.

(b) Fluorocarbons. At present, there are two popular fluoroethylene resins, polytetrafluoroethylene (Teflon)⁽¹⁾ and polymonochlorotrifluoroethylene (Kel-F)⁽²⁾. They are the most chemically resistant of the organic polymers and have excellent heat resistance. Kel-F has good heat resistance at 390°F; Teflon has good heat resistance at 500°F. Both have good properties at low temperatures. They are unaffected by sunlight, acids, and alkalies. Teflon is not attacked by organic solvents, but Kel-F swells slightly under influence of halogenated compounds. They are non-flammable, nonadsorptive to water and are resistant to fungi. They have excellent electrical properties. These resins are used for piping, handling corrosive liquids, and electrical insulation for high heat resistance. They are also used as a gasket material where corrosion and heat are encountered, as insulations of wiring in transformers, and as linings for tanks and vessels for handling corrosive liquids.

- (1) Tradename of E.I. DuPont de Nemours & Co., Inc.,
Wilmington, Delaware.
- (2) Tradename of 3M Company, St. Paul, Minnesota.

(c) Radiation Cross-Linked Plastics. Two radiation cross-linked plastics have found use as cable insulation in severe environments. In deep groundbeds, where gaseous reaction products tend to build up and react with traditional cable insulations, radiation cross-linked plastics have proven more effective. In particular, radiation cross-linked polyalkene and radiation cross-linked polyvinylidene fluoride are used for this purpose.

(d) Polypropylene. Polypropylene is lightweight and exhibits heat and corrosion resistance superior to polyethylene. This plastic retains strength at elevated temperatures to a greater extent than many thermoplastics. However, at low temperatures, it fails on impact more easily. Polypropylene is used for pipe, valves, fittings, containers that will be heated, and rope.

(e) Rigid Polyvinylchloride (P.V.C.). This plastic is fungi-resistant. It has high resistance to acids, alkalis, and alcohols, but is subject to light and heat deterioration. Without plasticizers, it is hard and makes a good durable material. When plasticized, it has a wide range of flexibility. Polyvinylchloride has very good electrical insulating properties and is used extensively as an insulating tape and as a protective covering in corrosive environments. It is also used for tubing, air ducts, and tanks containing corrosive liquids, and as a plastic paint, sheeting, and covering.

(f) Polystyrene. This plastic has some outstanding features: high refractive index, low specific gravity, good electrical properties, and resistance to water and chemicals. Modifications have been made to improve temperature-distortion characteristics. It is more brittle than most other thermoplastic materials; is soluble in esters, ketones, aromatic hydrocarbons, and carbon tetrachloride; and is subject to fungi attack. Polystyrene is inexpensive. It shows good resistance to attack by hydrofluoric acid. It is extruded and molded for light structural items of limited heat resistance to 100°C and is used for piping when polymerized with esters, as cast optical parts, and in electronic components. It is usually reinforced and laminated.

(g) Chlorinated Polyether. A relatively new plastic, chlorinated polyether is used in many corrosive environments, for coatings and linings and also for pipe and valves. It exhibits good corrosion resistance even to aggressive environments.

(h) Acrylics. The most important acrylic resin is methyl methacrylate. It has excellent optical properties, dimension stability, resistance to outdoor weathering, and chemical resistance. Heat-resistant formulations are available that can tolerate boiling water without distortion.

Methyl methacrylate is fungi-resistant, and, with some plasticizers, it has good resistance to bacteria and insects. It has good physical properties, but will degrade above 220°C by becoming unstable. It is used for structural sheets, clear plastic domes for aircraft, windows, instrument covers, optical parts, coatings, electronic components, water-dispersed water paints, and rigid piping. It is the principal resin in many clear plastic coatings.

(i) Polyamides (Nylon). These resins vary in composition and form; some are rigid and others are semi-flexible. They are practically inert to alkalis, organic acids, and most solvents; they have an extremely slow burning rate and are self-extinguishing. Tough and resistant to abrasion, they have good resistance to fungi and moderate resistance to mineral acids. However, they will rapidly disintegrate in cold, concentrated nitric acid and will absorb water, resulting in dimensional instability. They readily oxidize at high temperatures. At normal temperatures, oxygen, ozone, and sunlight have some degradation effect. Polyamide resins are used as electronic components, bearing materials, and nylon rope, as well as protective braid cover over insulated wire and power cables.

(j) Vinyls. Commonly-used vinyls are co-polymers of vinylchloride and vinylacetate. Saran⁽³⁾, a vinyl often used, is mainly vinyladenenechloride. These materials are used for tubing, pipe, phonograph records, fibers, and insulation.

(k) Acrylonitrile Butadiene Styrene (ABS). Use of ABS in industry is declining. It has been used for general oil field applications including pipe. This material is strong and tough, and heat stable. It is generally corrosion resistant, but cannot be used for handling most organic solvents.

(l) Cellulose Acetatebutyrate (CAB). CAB is one of the original plastics used industrially, but its use has declined greatly. This plastic has low moisture absorption and will resist weak acids, salt solutions, and aliphatic hydrocarbons. It is subject to swelling in alcohol and aromatic hydrocarbons and will dissolve in some esters, ketones, and chlorinated hydrocarbons. It has fair resistance to acids and alkalis, weathering, and aging. Such plastics have high impact strength and are tough; however, they may have a noticeable odor. Industrially, however, they were used extensively as pipe below grade for water and gas. They are made into flexible sheeting and are also used as coatings.

(3) Tradename of Dow Chemical Company, Midland, Michigan.

(2) Thermosets. Thermosets harden upon heating and remain hard when cooled. They cannot generally be reworked once set, because they undergo a non-reversible change in forming.

(a) Phenolics. Phenolics were one of the first plastics widely used as engineering materials. Usually they are derived from phenol formaldehyde, but other compounds are also used. Phenolformaldehyde resins as a class are fairly resistant to chemicals, fungi, heat, and light. They are not completely resistant to weathering for long periods. They can be molded, extruded, or laminated and are used as piping, electrical switch panels, switch handles, plates, pulleys, and insulation.

(b) Epoxy. These resins were first produced chemically during 1950 by reaction of bisphenol and epichlorohydrin. Resins in the uncured state are thermoplastic and range from low viscosity liquids to high melting point solids. Hardening of epoxy resin is accomplished by reaction with a curing agent at room or elevated temperatures. Amines, acids, and other resins are commonly-employed hardeners. Epoxy resins have excellent adhesion to metals, ceramics, glass, certain plastics, and wood, leading to their use as adhesives. The resins are used as surface coatings because of their wetting of, and adhesion to, a wide variety of different types of surfaces, and due to their excellent resistance to many acids, most alkalies, and solvents. In combination with coal-tar coatings, the paint retains the excellent qualities of coal-tar coatings with the abrasion resistance and hardness of epoxy resins.

(c) Ureaformaldehyde. These resins have moderate resistance to weather, acids, alkalies, common solvents, greases, oils, and hydrocarbon solvents. The molded resin is more resistant chemically than the laminated type, which contains fillers of cloth fabric or paper. It will absorb water to 1 to 2 percent. The laminated resin is used for table and counter tops. It is brittle, but cheap. A coal-tar urethane coating has been developed which has most qualities of urea resins and coal-tar coatings.

(d) Polyesters. Polyesters have a wide range of uses as reinforced material. They can be made as elastomers or rigid materials. They have fair abrasion resistance and are also resistant to most acids, bases, salts, and solvents. These resins are used as structural material when reinforced with glass cloth. They are also used for piping, fume ducts, hoods, large electronic components and boats.

(e) Silicon. The silicon resins are different from other plastics because they are based on a non-organic material - silicon. These resins can be used at high temperatures and have a negligible burning rate. They have low water absorption and are inert to fungi. They are slightly affected by weak acids and are resistant to oxygen over a wide range of temperatures. They have poor resistance to weak alkalies and are attacked by some aromatic solvents.

Silicon resins are made in liquid or solid forms and are used as rigid tubing for handling acids, particularly at high temperatures. They are used as corrosion-resistant coatings, and as electrical insulation on wires.

(f) Reinforced Plastics. Reinforced plastics are a widely used engineering material. They generally consist of thermoset plastic with cloth, wood, metal, or fibers such as fiber glass embedded therein. Such reinforcing gives the material tensile strength, while allowing the resin to retain its light weight. Fiber glass reinforced plastic (FRP) is often used for pipe, tanks and sheet (Figure 5-1) and has proven both strong and corrosion resistant.

b. Rubber and Synthetic Rubber. Natural and synthetic rubbers are not only very resilient, but they have other qualities useful in engineering materials. They are good insulators and exhibit chemical and abrasion resistance. In general, natural rubber is less corrosion resistant than synthetic, but has superior mechanical properties.

(1) Natural Rubber. Natural rubber is subject to deterioration by sunlight and is, therefore, compounded to prevent oxidation. A good rubber compound is highly resistant to chemicals, moistures, and serious fungi growth; but will deteriorate in alkalies, oils, fats, and ozone. Several natural rubbers are caoutchouc, Heava, and Guayule. They are used as a flexible cushioning material and for tires, tubing, gasketing materials, sheeting, lining, and footwear. They are also used in surgical apparatus.

(2) Synthetic Rubber. A number of synthetic rubbers are available, each having properties dependent on additives or chemical makeup. Some are combined with plastics to vary available properties.

Butadiene styrene copolymer (GR-S) is among the most widely-used synthetic rubbers. Varieties of this product are designated as Buna-S, Butaprene-S, Chemigum, Hycer-OS, and Nubun. Chemical resistance is similar to that of natural rubber. Such synthetic rubbers have greater biological resistance than natural rubber and have good resistance to aging. They are not immune to fungi and are subject to cracking on prolonged exposure to sunlight. They are used as electrical insulating material on wires and cables, and as binders in water-dispersed latex paint for inside use.

Isobutylene-diolefin copolymers (Butyl rubber or GR-I) can be vulcanized and are chemically inert. For many purposes, they are superior to natural rubbers. They are resistant to moisture, oxygen, ozone, and fungi, and have good abrasion resistance. They are also impervious to gases. They are used as weather-resistant covering over insulating rubbers; as tire walls; gaskets, where relatively high temperatures are involved; hose coverings; and linings. They are also used in insulating compounds.

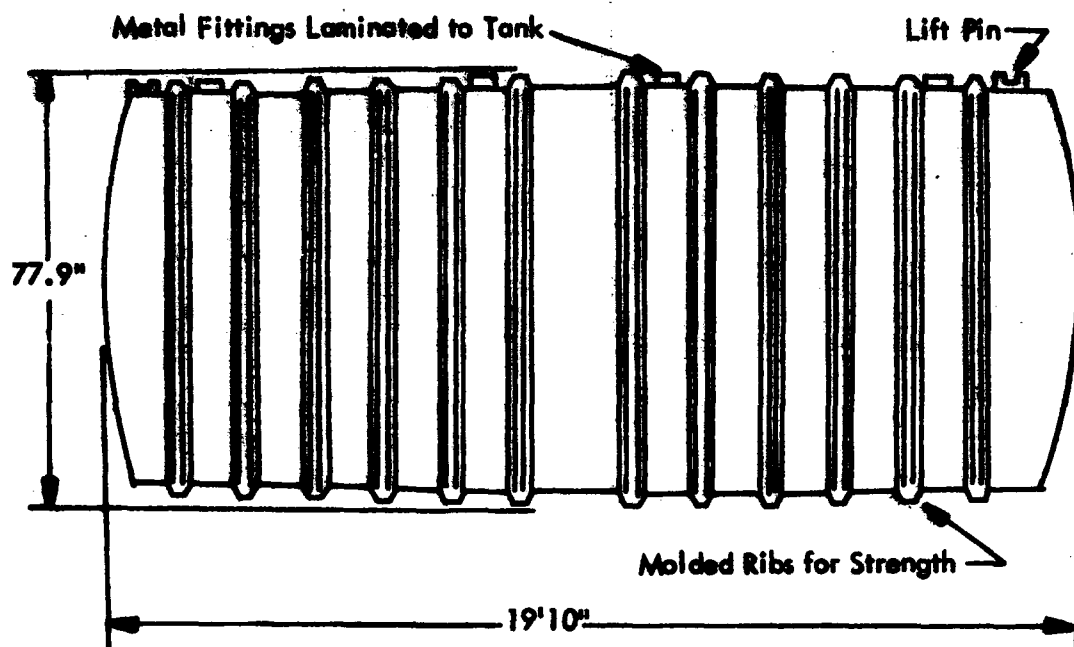


Figure 5-1
TYPICAL FIBERGLASS UNDERGROUND TANK

Neoprene (GR-N) was first developed in the early 1930's and came into prominence during World War II when natural rubber was held by the enemy. It is useful for handling strong sodium hydroxide and is resistant to aging, sunlight, heat, ozone, many chemicals, oils, and gasoline. It is used as linings for handling chemicals, oils, and gasoline; belting in contact with coal; electrical insulating material for wire and cable; and as maintenance paints that have good chemical resistance.

Nitrile rubbers (Buna-N), like neoprene, are resistant to oils and gasoline. In general, their chemical resistance is not as good as some other synthetic rubbers. Buna-N type rubber includes Perbunan, Hycar-OR, Chemigum-N, and Butaprene-N. Perbunan has good resistance to aging and high temperature. It remains flexible at very low temperatures and is used as gasket material in contact with oil, belting in contact with coal, and tubing in contact with oil or hydrocarbons. It is also used as diaphragms for valves and pump parts.

Organo-silicon rubbers (silicon rubbers) have good heat resistance, retain elasticity at temperatures of 500°F and are flexible down to -112°F. They have fair resistance to sunlight and many chemicals, but are not resistant to gasoline and many solvents. Their abrasive resistance is poor, and

their tensile and tear strengths are lower than for most natural and synthetic rubbers. They are used as: gasket material over a wide range of temperatures; tubing; caulking compound; and electrical insulating material.

In general, synthetic rubbers are diverse in corrosion resistance and other properties. Soft rubbers are generally preferred for abrasion resistance. When rubbers fail as a coating, often it is because it has become disbonded. Other factors such as elasticity, temperature resistance, and elongation should be examined when considering these materials.

c. Carbon and Graphite. Carbon and graphite show good resistance to many corrosive environments, including most acids and alkalies. Strong oxidizing acids and halogens will attack these materials, however.

Carbon and graphite are very brittle and much weaker than metals. Like metals, they exhibit good thermal and electrical conductivity and find use at high temperatures. These materials are used as impressed current anodes, in nuclear reactors, for pumps and heat exchangers.

d. Cement and Concrete. Cement and concrete are general terms describing numerous materials and a wide range of composition. Although cement compositions are fairly standardized, concrete specifications are far less rigid. Concrete may contain practically anything. Water, cement, and aggregate quality generally are location-dependent. The resulting properties also vary. Therefore, all applicable chemical properties should be known prior to use. For example, it is important to know pH of cement or concrete, as normally a pH of 5.5 is the lowest acceptable for engineering use. In addition, the various components of concrete or cement - sand, water, aggregate materials, and other additives - must follow strict specifications to prevent serious corrosion and mechanical properties.

Cement and concrete are not insulators. They will absorb moisture and, acting as electrolytes, conduct electricity. (This is a function of the material's density.) Corrosion of steel reinforcing bars in concrete is a consequence of this; rebar corrosion is discussed in paragraphs 5.3.3.1.e-f. Attempts to prevent this have been made with questionable success by applying various coal-tar coatings to surfaces in contact with corrosives.

(1) Asbestos Cement. Asbestos Cement is a mixture of Portland cement, fine fibers of asbestos, and water. Composition varies from 8 to 15 percent asbestos and from 85 to 92 percent cement. Asbestos fiber gives asbestos-cement higher tensile strength than concrete. It also has lower density. Consequently, less asbestos-cement is required for a given purpose than concrete, and the result is lighter in weight. The product is used for various purposes

including tiles, gutters and pipes.

As pipe, it is built up on a revolving mandrel and cured. Pipe of this type is largely used for water mains in the pressure range of 50 to 200 pounds per square inch. Concrete-encased asbestos-cement pipe is also used for ducts for electric power cables and communication cables. If the ground pressure is even and the backfill is not rocky, such pipe will give years of satisfactory service in most environments. Tests on asbestos-cement pipe that had been in soil for 13 years showed an initial gain in strength for several years as a result of continued slow curing taking place. After 13 years, there was a moderate loss of strength, but not to values below the usual specifications. Both organic and inorganic acidity in soil are moderately injurious to asbestos-cement pipe. It can be used with reasonably long life in bay muck, blue clay, and other soils highly corrosive to ferrous pipe.

e. Concrete. The grade of concrete termed "dense" is used for many tank and pipeline applications in mildly corrosive environments. For more destructive situations, concrete may be coated or lined. Concrete is composed of a bulk of coarse aggregate with sand or another fine aggregate filling voids. Watered cement bonds concrete together. Properties of concrete depend mainly on the "mortar" made of cement and fine aggregate.

Reinforced concrete contains steel bars embedded in it. Concrete both protects bars from corrosion and helps them to withstand any compressive stresses. If rebars do corrode, problems arise. Rust occupies 2.2 times the volume of iron, and such expansions cause spalling and cracking of concrete. Therefore, concrete quality must be good enough to prevent moisture and air from contacting reinforcement. Galvanized steel bars may also be used; zinc galvanizing protects steel sacrificially.

Admixtures or surface treatments may be used to alter properties of concrete. Many treatments are available, and combinations provide many forms of concrete with greatly varying properties.

Problems with concrete structures are encountered where frost prevails, in sea water, in sulfate-bearing environments, in acid soils and waters, with sugar waters.

Stray current causes corrosion of reinforced concrete. Current flows along rebars, leaving the surface through the concrete electrolyte. Corrosion occurs at areas where current leaves, producing voluminous rust products. Spalling and cracking of concrete follows. This is made more serious when chlorides and other soluble salts are in the environment but is less frequently observed in denser materials.

Petroleum distillates fuel oils, sewage, and gases generally do not seriously affect concrete. Concrete tanks and pipes are often successfully used in this service.

f. Prestressed Concrete. Prestressed concrete is reinforced concrete with rebars constructed from high strength carbon steel under high tensile stress. This type rebar is highly susceptible to stress corrosion cracking. Hydrogen embrittlement is also a problem, especially in acidic environments. Sea water and soils or solutions containing nitrates are environments to avoid.

Straining wires in prestressed concrete are often subject to extreme damage by stray current because of the small cross-section of metal. Calcium chloride, often used to increase hardness of concrete, may intensify effects of stray current and should, therefore, never be used in prestressed concrete. It is felt that calcium chloride also contributes to elongation and loss of strength of stressed reinforcing bars.

g. Vitrified Clay (Structural). Vitrified clay pipe, like asbestos-cement pipe, may be selected in certain phases of construction work to avoid corrosion problems. Vitrified clay is similar to concrete in properties but chemically more resistant. Vitrified clay is suitable for handling acid salts. It is often used underground for the same purpose as concrete pipe, primarily in non-pressure water service and sewage lines. It is also widely used to handle chemical and waste materials and may be made into ducts for underground cable.

h. Glass. Glass is a useful material for many applications because of resistance to most corrosives and ease of fabrication. Transparency is another property which makes it useful for a variety of equipment requiring visual supervision. Glass is used for piping, pumps, stills, tanks, and heat exchangers. Glass fiber embedded in plastics has already been discussed. These fibers are also used alone in insulation and air filters. Glass resists most corrosives; it is attacked by hydrofluoric acid and caustic alkalis.

i. Miscellaneous Ceramics. The most important ceramics - concrete, glass and clay - have been discussed previously. Others, such as stoneware and porcelain, are also used for construction. Every category of ceramics includes a wide variety of compounds, dependent for their properties on composition. Ceramics are basically made of metallic and nonmetallic components.

They are used most often in the chemical industry, because they exhibit good resistance to most chemicals. Exceptions are caustics and hydrofluoric acid. Ceramics withstand more abrasion and higher temperatures than most metals, but are weak and brittle. To add strength, ceramics used for

mechanical equipment such as pumps are often encased in cast iron.

j. Wood. Wood is used for filter presses, tanks, barrels, cooling towers and chemical equipment. This material is limited in its applications; usually water, dilute chemicals, and acetic acid are not destructive. Dilute alkaline solutions are harmful, however, to woods in general.

Soft woods, containing much cellulose, are used with different solutions than hardwoods, containing more lignin. Some chemicals attack only cellulose; some, only lignin. Pine, oak, redwood, and cypress are woods usually employed as non-building materials.

5.3.4 References to Codes and Regulations. Minimum requirements for pipe are contained in Title 49, Parts 191 and 192 of the Federal Code of Regulations (Department of Transportation), (adopted, 1969). These requirements are included as Appendix E. of this manual. In general, the code requires that pipe material remain stable for system temperature and environment and that it is chemically compatible with materials being transported. Qualifications for specific metals and plastics are noted also. This code can be used as a guideline by the military for proposed installations.

In addition, State and local requirements may limit the use of some materials (i.e. plastics) and should be considered.

5.3.5 Economics of Choosing a Material. Evaluation of properties required of a material for a specific application will usually indicate several appropriate materials. Economics may then be the final criterion in material selection. (See Section 2 for other criteria.) An analysis of economics of candidate materials will generally include:

- Material costs
- Fabrication costs
- Installation costs
- Maintenance costs
- Return on investment

These costs apply not only to materials, but also to related areas such as corrosion control requirements (paragraph 2.5).

5.4 COATINGS AND WRAPPERS FOR UNDERGROUND AND UNDERWATER.

5.4.1 Coatings. The oldest and most widely used corrosion remedy is coating. Structures are coated to minimize the possibility of contact with surrounding corrosive media. Most coatings do not completely cover any surface, but greatly reduce exposed area so as to make complete corrosion control feasible.

With increased use of metal underground and underwater, coating technology is important. The emphasis has been on developing a "perfect" coating to eliminate effects of holidays on coated metal. In practice, perfect coating rarely, if ever, exists, in spite of carefully controlled, automated coating procedures and complete electrical holiday inspection. As a result, the combination of good dielectric coating supplemented with cathodic protection is usually the most economical and efficient method of underground or underwater corrosion control.

Other coatings are often more effective than dielectrics for use above grade, with chemicals or for other applications, but dielectrics are the only long-term coatings effective underground or underwater. Special problems are encountered here which must be considered in choosing proper coating. Soil stresses from debris in backfill, non-uniform backfill pressure, or changing moisture content of soil can damage coating. Inaccessibility of buried or submerged structures necessitates using coatings with long life and few maintenance requirements; coating integrity should generally last for the life of the structure. Inspection should not be required to insure proper coating adhesion or integrity, since this is generally infeasible. Coatings for buried or submerged structures must be resistant to impact, both during and after installation, to avoid damage from accidental contact or deformation. Where other work is being done nearby, the existence of a buried or submerged structure may not be recognized until it is physically contacted. Environmental conditions must also be analysed prior to coating selection, for some environments can easily dissolve coatings. Asphalt-base coatings, for example, should be avoided where gasoline permeates soil. Coatings for use inside potable water storage tanks must be approved by the Food and Drug Administration; standards of acceptance are often changed and updated ones should be consulted. Likelihood of future contaminants, such as deicing salts or chemicals, must also be considered. Choice of a specific coating depends on these as well as other factors.

Coatings may be categorized in many ways. Here, they are considered either conductive or insulating (dielectric).

5.4.1.1 Conductive. Conductive coatings are metal coverings or claddings which protect base metal by two different processes, depending upon the position of the applied metal in the electromotive series. When the applied metal coating is more noble than the base metal, the coating will be cathodic and not corrode in the environment. This type is referred to as cathodic coating and cladding. For example, a thin layer of stainless steel over steel may increase structure life in a given environment several times over ordinary steel. Where applied metal is anodic to base metal,

it may corrode to protect the base metal. In such instances, the applied metal reacts with the surrounding electrolyte to provide cathodic protection. This type is referred to as anodic coating and cladding. For example, a zinc coating on steel will corrode to protect steel; an aluminum cladding on an aluminum alloy will corrode to protect the aluminum alloy.

Structures that require ferrous alloys for strength but face rapid failure from corrosive conditions can be coated to yield the corrosion resistance of a more passive metal. In addition, savings will be realized through longer life, which may offset the additional cost of plated or clad material.

Plated or clad structures have the advantages of corrosion resistance and freedom from maintenance. Usually painting and other maintenance required on steel structures are not necessary on plated or clad metals. This is frequently a major consideration. On the other hand, plated or clad materials may not be immediately available when needed, and may involve installation by specially trained personnel. Thus, additional first costs of material, fabrication, and installation must be considered against savings from corrosion and maintenance.

a. General. Information on coatings (not underground or underwater) is found in military manuals on Paints and Protective Coatings. These manuals should be consulted for general information on selection and application of above-ground coatings not discussed here.

(1) Cathodic Coatings.

(a) Nickel and Chromium. Nickel is corrosion resistant as well as ornamental. It is used extensively for plating instrument cases, trim on automobiles, plumbing fixtures, storage tanks, and vessels that contain caustic solutions. Chromium is used as a protective and ornamental coating on tables and kitchen utensils over a plate of nickel. Chromium is also used as a plate or cladding on metals for wear and oxygen resistance.

(b) Copper. Copper cladding is used on steel wire for electrical conductors. It is corrosion resistant to most atmospheric conditions. In comparison to solid copper wire, the primary advantage of copper-clad steel wire is increase in structural strength, which makes possible the use of long spans in overhead power lines. Copper is also used as a cladding for nails and other hardware.

(c) Tin. A tin-nickel alloy (Sn, 65 percent; Ni, 35 percent) is used extensively as cladding for food containers and plating for kitchen utensils. Because it will prevent corrosion of copper, a tin-nickel alloy is also used as cladding for copper wire that is to be insulated with rubber.

(d) Tantalum. Tantalum is used as plate or cladding for vessels or pipe when other metallic materials, even gold and platinum, cannot be used because of an environment favorable to corrosion. Chemical properties of tantalum closely resemble those of glass. Tantalum is rapidly attacked by hydrofluoric acid and by strong, hot alkalies. It is also attacked by fuming sulfuric acid or other substances containing free SO_3 .

To a lesser extent, tantalum is attacked by hot concentrated sulfuric and phosphoric acids. For certain commercial applications, however, even with such acids, tantalum has given satisfactory long life. Because tantalum is virtually inert to all other acids or acidic salts, it is a suitable lining material.

(e) Cadmium. Cadmium, used to coat metal, is generally applied as plating. Cathodic to steel and iron, it does not protect bare areas or breaks in coating. It is extensively used for atmospheric coating due to the bright finish produced and is excellent for thin plating thickness which cuts plating costs.

(f) Stainless Steel. Various types of stainless steel are used as cladding for steel to produce vessels which have the corrosion resistance of stainless steel at a cost not much greater than steel.

(2) Anodic Coatings.

(a) Zinc. The most commonly used anodic coating is zinc, which may be applied by four methods: plating, sherardizing, hot dip, and metallizing. Zinc-rich paints are also used for certain applications, but are not discussed here (AFM 85-3, Paints and Protective Coatings).

Zinc is applied to iron, steel, magnesium, or aluminum by electroplating. The metal to be plated is made the cathode in an electrolyte containing zinc. Zinc is the circuit anode. Zinc plating is used where hot dip would interfere with proper use of such articles as nuts, bolts, and other threaded parts and to reduce total zinc used by producing a uniform thin coating on plate or sheet.

In sherardizing, zinc is applied to steel or iron by cementation. Characteristic of this process is alloying of the metal surface with zinc. The sherardizing process consists of cleaning and pickling (or sandblasting) the metal surface before treatment. Clean metal is placed in drums or retorts containing zinc dust. The drums are rotated at slow speed for three to four hours at about 750°F (400°C). The resultant coating is a zinc-iron alloy. Sherardized coating is porous and usually painted, varnished, or enameled, for uniform distribution and penetration.

The hot-dip process is used extensively for galvanizing iron or steel. Facilities are necessary for pickling, washing,

and application of flux. Steel is dipped into molten zinc at a temperature of about 875°F (468°C). A good coating is about 2 ounces of zinc per square foot of coated area. Addition of a small amount of aluminum to the hot baths of zinc improves fluidity and coating appearance.

Steel and iron can be coated with sprayed molten zinc. Zinc is fed as wire into a metallizing gun. The oxyacetylene flame melts the zinc and projects it as an atomized spray on the surface to be coated. The metallized surface has a rough, porous coating which makes an excellent bond for paint or organic coatings.

(b) Aluminum. Aluminum is generally applied by two methods: cladding and hot dip. Aluminum paints are also available, but are not discussed here (Military Manuals on Paints and Protective Coatings).

Pure aluminum is applied by rolling sheet aluminum on the surface of a strong aluminum alloy. Pure aluminum is anodic to the aluminum alloy and protects it galvanically.

Aluminum is also applied to steel in a manner similar to galvanizing. This is usually a continuous process with steel sheet fed through descaling and cleaning baths, flux and molten aluminum, and emerging with an aluminum coating. Aluminum, anodic to steel, performs like zinc galvanizing. Aluminum-coated steel also has excellent oxidation resistance up to 800°F. The aluminum oxide coating formed on aluminum keeps oxygen from contacting the metal.

b. Underground and Continuously Submerged. Copper and zinc are the most common underground and underwater metallic (conductive) coatings. These are described above. Copper, a cathodic coating, is used on ground rods and bolts underground. It is not recommended as a cladding underground for pipe or tubing because any cut or abrasion exposes steel, creating an anode. Because of the difference of potential between copper and steel in the galvanic series, accelerated corrosion of steel occurs when the two metals are in an electrolyte. For example, accelerated corrosion takes place when such pipe or tubing is encased in concrete floor slabs, such as for radiant heating, permeated with moisture.

Zinc galvanizing, anodic to steel, is sometimes used underground or underwater. However, galvanizing usually corrodes away rapidly, leaving bare steel in contact with a corrosive environment. Protection from zinc is proportional to its thickness, and coatings with enough metal to provide a good life are generally prohibitively expensive.

5.4.1.2 Insulating (Dielectric). Dielectric protective coatings are used extensively in corrosion control. They

are especially effective underground, in conjunction with cathodic protection. The purpose of these materials is to electrically isolate metal from its environment by maintaining a moisture-resistant seal between the two. Quality coating is judged by its ability to resist moisture absorption, although mechanical strength and chemical resistance are also important factors.

Underground insulating (dielectric) coatings are discussed in detail in paragraph 5.4.1.2.a. Others are mentioned here. For further reference to above-ground insulating coatings, see AFM 85-3, Paints and Protective Coatings.

Among coatings frequently employed are conversion coatings. These are formed by reaction of the metal surface with a chemical and are in reality a surface layer of adherent reaction product. There are many methods of applying or producing conversion coatings, resulting in a variety of properties. Perhaps the most common is anodizing - deposition of material on metal, producing an intermediate layer of base and deposit material in complex. The coating material is generally deposited by electric current from an aqueous solution. Such reactive metals as magnesium and aluminum are frequently anodized. Anodized coatings are generally hard and adherent, easily and uniformly applied to complex shapes, and resistant to many corrosives. Other conversion coatings include calorizing, aluminizing, and phosphatizing.

Glass-lined or coated vessels are used with chemicals or foods for their resistance to acids and alkalies and ease of cleaning. Glass coatings, also described as porcelain or vitreous enamels, are applied from a slurry, and are difficult to repair.

Concrete is an effective coating for steel in the atmosphere. Care must be taken to assure that voids are cement-filled, and that concrete is well-mixed. Reinforced concrete has failed from rebar corrosion due to improper mixing. Reinforced concrete fails more rapidly in sea air than if submerged, producing bridge and other failures (paragraph 5.4.1.2.a(6)). Concrete should not be used with amphoteric metals such as aluminum or lead because it is alkaline.

Plastics applied by dipping, spraying, or fluidized bed processes constitute another group of above-ground coatings. Some plastic film-type coatings (as differentiated from tapes, discussed in paragraph 5.4.1.2.a), require a primer; some, a catalyst for curing. The large number of plastics available result in a variety of properties for different uses. Both thermosets and thermoplastics are used.

Inhibited greases are also used for coatings, sometimes covered with a wrapper for protection. Often, greases are used

for temporary protection during storage or in transit. These materials leach away after continuous exposure to moisture.

It is important to realize that any coating material is only as good as its application. The first step in good application is surface preparation. After good surface preparation, coating must be applied carefully in accordance with specifications to assure satisfactory results.

a. Underground. The National Association of Corrosion Engineers Standard RP-01-69, Recommended Practice - Control of External Corrosion on Underground or Submerged Metallic Piping Systems, contains a discussion on "installing of piping systems coated with electrically insulating materials". This is valid for most submerged or underground structures, not only pipelines. It states:

"The function of such coatings in corrosion control is to isolate the external surface of underground and submerged piping from the environment. This can be substantially accomplished by different types of coatings. These coatings can be formed on the pipe surface or prefabricated as films or wrappers and then applied ...

Desirable characteristics of coatings:

- (a) Effective electrical insulator
- (b) Ease of application to pipe
- (c) Applicable to piping with a minimum of defects
- (d) Good adhesion to pipe surface
- (e) Ability to resist development of holidays with time
- (f) Ability to withstand normal handling, storage and installation
- (g) Ability to maintain substantially constant electrical resistivity with time
- (h) Resistant to disbonding when under cathodic protection
- (i) Ease of repair".

Several coating systems exhibit these properties. To rely on an insulating coating as the only means of corrosion protection, however, requires a "perfect" coating, completely free of holidays. In practice, this is rarely, if ever, accomplished.

"Holidays" (breaks in the coating) are inevitable. They are caused in most coatings from incomplete coverage during application and/or damage during handling, installation, and service. Holidays can be detected either before or after burial and repaired. After burial this is expensive and often not practical.

Coating alone, as corrosion protection, can result in more rapid corrosion penetration of metal than if bare. Coating limits areas from which corrosion currents can flow, concentrating corrosion at limited areas of exposure.

The most significant advantage of dielectric coating is reduction in metal surface area exposed to soil or water. This reduces cathodic protection current requirements, minimizing costs. Coating and cathodic protection is a long accepted and proven system of underground corrosion control. Bonded coatings must be applied carefully because cathodic protection may not work under unbonded coating.

Corrosion cannot occur on a buried metal structure where coating physically adheres to metal. It can occur only where this bond is broken, but it is not limited to areas with direct soil exposure. Severe corrosion can occur in the moisture film under an unbonded coating, even though potentials between structure and electrolyte show adequate protection is being applied. Entrapped moisture between coating and structure surface may promote corrosion despite cathodic protection. Therefore, good coating techniques must be used to prevent increased corrosion at breaks, holidays, or disbonded areas.

The most common and successful coating materials for underground and underwater are hot tars - hot-applied coal-tar enamel or hot-applied asphalt coatings used with wrappers and reinforcement. Both have long-term service records for effectiveness underground and underwater. Hot-tar coatings may be field-, yard- or mill-applied to pipe. For field-coating, method of surface preparation and application are similar for either type coating. Typical specifications for coal-tar field-application are given in paragraph 5.4.1.2.a(1). Hot-applied coal-tar coatings are most frequently used with wrappers for external coatings for steel pipelines and other underground structures, but also find application as interior linings in both steel and concrete lines.

In recent years, extruded polyethylene (paragraph 5.4.1.2.a(4)) and thin-film coatings (paragraph 5.4.1.2.a(7)) have become more popular for use underground. These coatings appear to give satisfactory service, although their recent introduction precludes long-term service records.

Other underground coatings, some for specific uses, are discussed here also.

(1) Hot-Applied Coal Tar. Hot-applied coal-tar (coal-tar enamel) consists of molten bituminous coal-tar pitch reinforced with inert fillers such as lime or slate dust and applied by hand or machine, over a primer. (For reference see AWWA 8310-D Committee Report "Standard for Coal-Tar Enamel Protective Coatings for Steel Water Pipe - AWWA-C203" and NACE 2G156 Report "Coal-Tar Coatings for Underground Use".) The coating may be reinforced with embedded glass mat and/or outer wrapper of glass mat or asbestos felt saturated with a compound made from the basic coal tar. Over this, a covering of kraft paper or whitewash may be added. Average coating thickness is 3/32" to 5/32".

Primers used with coal-tar enamel are either a "cutback" of the type coal-tar used or a synthetic, paint-like substance. (For reference see U.S. Government Printing Office Publication "Synthetic Resin Primer for Coal-Tar Enamel", Research Report No. 8, U.S. Dept. of the Interior, Bureau of Reclamation.) Synthetic primers are in general use today. Primers made from coal-tar cutbacks are less practical; they are difficult to apply, and drying time is critical. For any primer, structure surface must be clean and dry prior to application. Typical specifications for a synthetic primer are:

	<u>Minimum</u>	<u>Maximum</u>
Weight, per gallon, lbs. at 77°F, ASTM D-1475	8.5	9.0
Total solids, % by weight ASTM D-1644	30	40
Viscosity, Stormer, seconds 75 gm.wt. ASTM D-856	20	40
Flash point, °F, ASTM D-1310	92	
Coverage, sq.ft. per gal.	800	1000
Dry time, minutes (exterior, summer)	3	

Coal-tar pitch is produced by distillation and dehydration processes from bituminous coals. Pitch is a thermoplastic containing the least volatile compounds, mostly aromatics, from coal-tar products. Production includes heating to about 2000°F, which imparts chemical inertness to coal-tar pitch. Variations in temperature and source of coal yield pitches at different characteristics; consequently, raw material quality and manufacturing methods are important to the final product. Removal of possible corrodents from pitch, plus addition of reinforcing fillers, improves the coating. In areas of severe soil stress or temperature variation (such as long periods of above-grade storage before use), more flexibility is needed, so a more plastic

enamel is required. Variation in filler content and quality of pitch affect flexibility. Three different grades of hot-applied coal-tar coating with different flexibilities are commonly used: standard, semi-plasticized and fully plasticized. Primers made from cutbacks of the specific type are used with each, or a synthetic primer can be used for all.

(a) Standard. Typical specifications for a standard coal-tar enamel are:

	<u>Minimum</u>	<u>Maximum</u>
Specific gravity, 77°F - ASTM D-71	1.40	1.60
Percent ash by weight - ASTM D-271	20	27
Penetration - 100 gm.wt., 5 sec., 77°F - ASTM D-5	0	2
Softening Point, °F, ASTM D-36	195	205
Temperature exposure range, °F	25	115
Normal application temperature, °F	340	390

Methods of preparing metal surface and applying coating are the same for standard coal-tar enamel and other hot-applied coatings. An example of specifications for application is given for fully-plasticized type coating, as this is the most applicable to underground structures (paragraph 5.4.1.2.a(1)(c)).

(b) Semi-Plasticized. Typical specifications for a semi-plasticized enamel are:

	<u>Minimum</u>	<u>Maximum</u>
Specific gravity, 77°F	1.40	1.60
Percent ash by weight	20	27
Penetration - 100 gm.wt., 5 sec., 77°F - ASTM D-5	2	7
Softening Point, °F	195	205
Temperature exposure range, °F	10	130
Normal application temperature, °F	355	400

Again, see paragraph 5.4.1.2.a(1)(c) for typical application specifications.

(c) Plasticized. Typical specifications for coating and wrapping a pipe with fully-plasticized coal-tar enamel for underground service are given here. These specifications may be used as a guideline for coating and wrapping with other coal-tar enamels or hot-applied asphalt.

Plasticized Coal-Tar Enamel Coating Systems.

A plasticized coal-tar enamel coating system shall consist of one coat of synthetic primer, a 3/32" minimum thickness of plasticized coal-tar enamel, and a glass fiber or 15-pound asbestos felt wrapper. The primer shall be compatible with the coal-tar enamel coating and shall be a resin-based, synthetic, "quick-drying" primer. The coal-tar enamel used for pipe coating shall have the following general properties:

Specific Gravity	1.4 to 1.6%
Percent Ash by Weight	35% Maximum
Penetration - 100 gm.wt., 5 sec., 77°F - ASTM D5-52	7.0 mm Maximum
Softening Point	220°F Minimum
Temperature Exposure Range	-10°F to 160°F
Application Temperature	450°F to 490°F

The wrapper shall be either 15-pound coal-tar saturated asbestos pipeline felt composed of inorganic nonrotting asbestos fibers or an inorganic nonrotting mat of fine glass fibers held together by a binder. Mill-coated coal-tar enamel coating systems shall have an additional outer wrapping of sulfate kraft paper.

Field Application and Inspection (With Electrical Inspection)

Short lengths of pipe, bare pipe ends, joints, and fittings shall be field-coated during construction of the pipeline. The coating shall consist of a thin coat of "synthetic" type primer for hot coal-tar enamel, followed by two coats of plasticized coal-tar enamel and a wrapper (bonded to the last coat of coal-tar) of 15-pound coal-tar saturated asbestos felt or glass fiber. The pipe shall be cleaned until free from all loose mill scale, rust, moisture, welding scale, dirt or grease. Grease or heavy oil shall be removed with an approved volatile solvent (not gasoline). If necessary, moisture shall be removed by preheating the pipe. After cleaning, primer shall be brushed on in a thin, even coat. Runs, drips or flooded areas in the finished priming coat shall be removed by brushing. The primer coat shall be dry before enamel coating is applied. (To test for dryness, scrape a small quantity of primer from the pipe and squeeze tightly between the fingers - dry primer will not stick to the skin.) Two coats of enamel shall then be applied to the clean, dry, dust-free primed pipe surface. Application temperature of the enamel shall be in accordance with manufacturer's specifications, taking into consideration the atmospheric temperature, weight of pipe, and conditions of application. Two coats of coal-tar enamel shall be applied by hand-daubing or "pouring and ragging", to a minimum 3/32" thickness. Application of the second coat will be followed by immediate wrapping with the 15-pound felt or glass wrapper so that the wrapper is bonded to the coal-tar coating. Wrapper overlap shall not be less

than one (1) inch. All coating shall be visually inspected for holidays and breaks during construction. Electrical tests shall be conducted in the field with a portable high-voltage, low-amperage holiday detector, in the following manner:

1. Electrical equipment used to test the enamel in the field shall be the portable, low-amperage, adjustable voltage, pulse-type holiday detector. The holiday detector shall be furnished with a coil spring electrode for the larger coated pipe areas and a suitable brush type electrode for the smaller coated bolt and structural surfaces. The applicator will provide an operator for this equipment.
2. The operating voltage of the detector shall be in the range of 8,000 to 15,000 volts. Due to variables such as relative humidity and temperature, the detector voltage shall be adjusted twice daily; just before starting work in the morning and just before starting work in the afternoon.
3. The operating voltage of the detector shall be determined by the following procedure:
 - a. Select a coated and wrapped portion at the overlap of the felt approximately 15" from the end of one pipe length. This location is required because it represents the maximum thickness of coating and wrapping on the pipe.
 - b. Deliberately puncture the coating and wrapping with a sharply-pointed tool.
 - c. Move the electrode back and forth over the puncture and reduce voltage until the detector does not indicate the known holiday.
 - d. Place a strip of dry 15-pound coal-tar saturated asbestos pipeline felt over the known holiday. Move the detector electrode back and forth over the felt strip, and slowly increase voltage until the detector starts to indicate the known holiday under the felt strip.
4. After voltage has been properly adjusted as outlined above, the electrode shall be passed over the coated and wrapped surfaces, one time only, approximately 35' to 50' per minute.
5. Evidence of holidays or missed places will be indicated by an electric spark between the electrode and the metal surface.

The Contractor shall provide electrical inspection equipment and an operator. Coating imperfections shall be marked for patching prior to backfilling. If no electrical inspection is used, all coating shall be visually inspected for holidays and breaks during construction. Coating imperfections are to be marked for patching prior to backfilling.

Repairing Damaged Coating

All holidays or breaks in coating shall be repaired before backfilling. Small holidays are to be repaired by pouring hot coal-tar enamel directly on the holiday. Breaks or holidays larger than 1" are to be patched by removing all unbonded coating and wrapper around the holiday. This area shall be repaired in the same manner as field application of coating.

Storage and Handling of Field-Coating Materials

Materials for field-coating and patching shall be stored and handled in a manner that prevents damage or contamination. All rolls of wrappers shall be stored on end in a dry place, kept from contact with concrete flooring, and protected from weather. Primer and coating shall be kept in containers that prevent contamination with dirt, grease, oils, and other foreign materials. Brushes used for the application of primer shall be clean and suitable for applying a thin, even primer coat. Kettles and containers used for heating and pouring coal-tar coating shall be free and clean of foreign material and dirt. Coating and wrapping materials shall be hauled in a manner that will prevent damage to the packages. The Contractor will be billed for excessive material damage and losses.

Handling Coated Pipe

Pipe shall be handled, shipped and stored in a manner that will prevent coating damage. Mill-coated pipe shall be stock-piled on soft ground or padded skids at the construction site. Coated lengths of pipe shall be handled with equipment equipped with rubber or canvas belt slings of sufficient width to protect the coating. Rolling or dragging the pipe over rough terrain is prohibited. Skids used in over-the-trench construction shall be padded with sand or straw bags, foam pads or suitable rubber padding. Lowering pipe into the trench shall be done only after the coating is thoroughly cooled. Care shall be exercised during lowering operations to avoid coating damage by sides of the trench, tree roots, and objects protruding from the trench wall. Before lowering, the trench bottom shall be inspected for rocks, skids, welding rods, and other debris that will damage coating. Removal of water from the trench may be necessary to perform this visual inspection of the trench bottom. Sliding and positioning the pipe in the trench is to be avoided and should be done only when absolutely necessary. An extremely dry or rough trench bottom shall be flooded with water to provide a smoother sliding surface and prevent excessive coating damage.

Backfilling Coated Pipe

Backfilling shall be performed in a manner that will prevent damage to the pipe coating. Rocks, stones, brickbats, and other hard debris shall be removed from the backfill adjacent to the pipe. In cases where rock or gravel is encountered in the bottom of the trench, the bottom shall be padded with soil or sand to a depth of four (4) inches. Where suitable soil or sand padding is unavailable, coated pipe may, upon approval, be protected from rock or gravel with a wrapper or layer of 3/16" thick pipeline rockshield. Finer portions of backfill shall be used for the first layer of backfill to a height of four (4) inches above the top of the pipe. Foreign materials and items common to pipeline construction, such as cans, buckets, skids, and welding rods, shall not be discarded in the trench.

(2) Hot-Applied Asphalt. Hot-applied asphalt coatings consist of air-blown asphalt reinforced with finely-divided mineral filler. (For reference see NACE 2H158 "Asphalt Type Protective Coatings for Underground Pipelines" or NACE 2H157 "Asphalt Type Protective Coatings for Underground Pipelines - Wrapped Systems" or the Asphalt Institute Publication "Asphalt Protective Coatings for Pipelines - Construction Series No. 96 - Wrapped and Mastic Systems".) Typical specifications for hot-applied asphalt are:

	<u>Minimum</u>	<u>Maximum</u>
Weight, lb./gal. at 60°F	---	10 ---
Percent Ash by Weight -	15	25
ASTM D-271		
Penetration - 100 gm.wt.,	4	10
5 sec., 77°F -		
ASTM D-5		
Softening Point, °F,	235	255
ASTM D-36		
Temperature Exposure	0	160
Range, °F		
Normal Application	450	500
Temperature, °F		

As with hot-applied coal-tar, hot-applied asphalt has a long-term record of effectiveness for underground service. It is applied similarly, over metal surface primed with an asphalt base primer and may include reinforcing glass wrapper and/or glass fiber or asbestos felt outer wrap. Mill-wrapped pipe will also be covered with kraft paper or whitewash. The specifications for surface preparation, application procedures, and handling and backfilling pipe coated with coal-tar enamel may be used as a guideline for asphalt enamel also.

Manufacturing method and raw material quality are important to a good asphalt enamel. Asphalt is produced by distillation of asphaltic petroleum or is mined directly as naturally occurring asphalt (such as gilsonite). The properties of distilled asphalt vary with raw material makeup, distillation time and temperature, and method of sparging. Air-blown, rather than steam-sparged, asphalts go into asphalt enamel. Addition of gilsonite to distilled asphalt often greatly improves its quality as a coating. Mineral ash is added for improved strength. Improved, modern asphalt enamels are less water-absorbent than predecessors, and are comparable to coal-tar enamels as coating for underground and underwater service. One disadvantage is lower resistance to petroleum products; asphalt coatings may be dissolved in environments containing such materials and their use there should be avoided.

(3) Asphalt Mastic. Asphalt mastic describes selected sands, fibers, and mineral ash held together with an asphalt binder. (For reference see NACE 2H158 "Asphalt Type Protective Coatings for Underground Pipelines" or NACE 2H257 "Asphalt Type Protective Coatings for Underground Pipelines - Mastic Systems" or the Asphalt Institute Publication "Asphalt Protective Coatings for Pipelines - Construction Series No. 96 - Wrapped and Mastic Systems".) These materials are applied hot, by pressure-extrusion techniques and are characterized by greater thickness than more conventional coatings. Average thickness of 1/2" to 5/8" are common, with thickness up to 1" available. Composition varies depending on service temperature requirements, but binder content of about 12% is common. Method of application includes preheating the pipe to dry the surface, thoroughly cleaning the surface, and applying hot primer. The coating is then mill-applied in a continuous process and coated with whitewash. Field-patching, especially in adverse weather conditions, can be a problem.

Asphalt mastic coatings are characterized by good coating integrity due to extra thickness. No outer wrappers are required. The coating's thickness gives it a special advantage in congested areas where contacts must be avoided even in close clearances. However, as with other asphalt coatings, care must be taken to avoid dissolution of mastic binder in environments containing petroleum products.

(4) Extruded Polyethylene. An extruded polyethylene pipe coating system consists of a hot film of high-density polyethylene extruded over a layer of hot, rubberized thermoplastic adhesive. (For reference see NACE 2K161 "Prefabricated Plastic Films for Pipeline Coatings".) Application procedure includes preheating of pipe to drive off moisture, cleaning, application of adhesive, extrusion, and water quenching. This type coating is most applicable to small-diameter distribution pipe. Joints are made with

shrunk-on polyethylene sleeves or tapes. Typical specifications for a polyethylene coating system are:

The system shall consist of a 10 mil layer of adhesive mastic and a 25 to 40 mil thickness of extruded high-density polyethylene. The adhesive mastic is to be a modified rubber-blend material that does not become hard or brittle. Extruded high-density polyethylene shall have the following general properties:

Tensile Strength	3,500 psi Minimum
Elongation	100%
Penetration - 200 psi load, 1/4" blunt rod	Negligible
Moisture Absorption	.02%
Dielectric Strength	1,000 volts per mil thickness

Polyethylene coating systems can be mill-applied to pipe from 1/2" nominal diameter to, and including, 10-3/4" outside diameter.

Also available are extruded coatings of polypropylene copolymer.

(5) Weighted Coatings. Weighted coatings consist of heavy material applied to pipe over the protective coating to provide adequate weight in water or non-stable back-fill. These coatings are generally concrete containing a heavy aggregate such as cast iron, reinforced with wire mesh. Coating composition and thickness are determined by required weight and environment. Weighted pipe is often difficult to cathodically protect, since metal reinforcing must not contact the pipe at any point. Contact results in shielding pipe from protective current. In addition to preventing contact, care must be taken not to damage protective coating during application of weighted coating. Once applied, weighted coating provides mechanical protection to the metal and protective coating, greatly reducing damage and the need for repairs.

(6) Concrete. Concrete or cement is used for both internal and external coating, especially on such structures as buried or submerged ferrous water or sewer lines, bridge supports, etc. Tight specifications of all ingredients, including additives, are required. Reinforcing mesh is usually used, especially on large diameter pipes. Concrete coating requires curing, usually several days.

Concrete is an alkaline environment and should not be applied to amphoteric metals such as lead or aluminum. However, this alkalinity causes ferrous metals to become cathodic, protecting them from corrosion. Pinholes or small cracks in concrete coating generally do not cause problems because they fill with alkaline material, preventing corrosion. Where larger sections of concrete break away from the metal surface, corrosion can occur at an increased rate.

Uncoated areas are anodic to those contacting concrete. This has been a problem with bridge support piles. On water crossings, piles are frequently encased in concrete from the deck to a point below water level. Severe corrosion has been found just below the jacket bottom, particularly in salt water. Concrete jackets should extend into the bottom, especially if cathodic protection is not used.

Another serious problem with concrete-surrounded structures is corrosion of reinforcing steel, producing spalling. The main cause of reinforcing steel corrosion is presence of chlorides in concrete. Chlorides are introduced into concrete in several ways. Sometimes they are used to accelerate curing; deicing salts are another source. Finally, salt water has been used in the past in coastal areas in mixing concrete.

The effect of chlorides is two-fold, in that both the pH and the electrical resistivity of the concrete are lowered. Normally, the pH of concrete is 12 or 13, and steel usually becomes passive in environments having a pH greater than 11.5. With addition of chlorides, however, the pH of concrete may drop to 6 or 7, in which range steel will corrode readily. Chloride-free concrete has a high resistance to flow of electric current but, with addition of chlorides, the resistance is lowered five- to ten-fold, again enhancing corrosion.

There are several remedies for reinforcing steel corrosion, some of which may be used together. Coatings, both metallic and dielectric, have been utilized. Non-sacrificial coatings such as copper or nickel provide a barrier between concrete and steel. Nickel has been quite successful, but with copper, if a break occurs, the steel substrate corrodes rapidly. Galvanizing, a sacrificial zinc coating, has been used with considerable success. Galvanized rods have an appreciably longer life than bare rods.

Dielectric coatings such as epoxies and bituminous materials, as well as cement slurries, are also used to control corrosion of reinforcing bars.

One of the most effective steps that can be taken is to prohibit the inclusion of chlorides in concrete. Low porosity concrete reduces corrosion, as does air entrainment. Adequate cover is essential and, where possible, a minimum of three inches should be specified.

Some experimental work has also been done on application of cathodic protection to reinforcing, but this is currently a theoretical area. Current density must be limited to minimize the possibility of losing bond between steel and concrete.

(7) Thin Films. A recent addition to the selection of underground coatings is the "thin film" group - coal-tar epoxy, butadiene styrene, or vinyl resin applied to a thickness of 8 to 10 mils. Some of these coatings are exceptionally tough, and can withstand physical treatment that could damage thick, more traditional coatings. (For reference see NACE publication "Recommended Practices Associated with the Application of Organic Coatings to the External Surface of Steel Pipe for Underground Use".)

(a) Coal Tar Epoxy. The first practical "thin film" coatings for underground pipelines were the coal tar epoxies - epoxy resins combined with coal tar or coal-tar pitch. Epoxy resins are the product of a condensation reaction, usually between bisphenol A and epichlorohydrin. The resultant resins vary greatly in molecular weight, depending mainly on system temperatures and pressure, and ratio of reactants. Low molecular weight epoxy resins are liquid; those of high molecular weight are solids. The resins contain unreacted epoxy and hydroxyl radicals in their structure and can be combined with coal tar and certain other materials without producing harmful byproducts. The resultant reaction causes crosslinking of epoxy resin molecules, with greatly altered properties.

Coal-tar epoxies may also contain curing compounds, mineral fillers, or solvents. The ratio of coal tar to epoxy resin may vary from 1:1 up to 3:1.

Coal-tar epoxies are an improvement over either major constituent for coating. Coal tar improves water resistance and greatly reduces cost of pure epoxy resin. Coal tar gains better resistance to many oils and solvents, improved thermoplastic properties, and better weathering characteristics. The combination yields a durable coating for both metal and concrete for underground and underwater applications. To prevent holidays, two coats should be applied; however, for many applications one coat suffices. Abrasion and impact resistance are excellent, as is adherence and resistance to soil stress. Use of coal tar epoxies in the presence of strong solvents, however, should be avoided.

Typical specifications for coating steel with coal-tar epoxy are given here:

Specification for Coating with Coal-Tar Epoxy

Coating System

a. The coating system shall consist of grit-blasting conforming to the specification below and following coating system:

- (1) One or two coats of coal-tar epoxy.
- (2) Material shall be applied by spray.

Preparation for Coating

- a. In planning the work, provision should be made for accomplishing the work in spite of obstacles caused by weather and other local conditions.
- b. Where work is to be done in winter months in southern latitudes and application must be made during very cold weather, provisions should be made for doing the work indoors in a heated space, if possible, to reduce the cost of the coating operation to a minimum.

Surface Preparation

- a. All surfaces to be coated shall be dry grit-blasted to a gray Commercial Blast at least equal to Steel Structures Painting Council Specification 6-52T with the additional requirement that all mill scale must be removed. Mill scale binder need not be removed.
- b. All work blasted in one day must be coated on that day and before dew point has been reached. Any blasted area, not coated, which is exposed overnight has to be at least whip-blasted before coating application.
- c. All areas of the surface which are to be blasted which show any trace of oil or grease shall be degreased, using naphtha or xylol prior to grit-blasting.
- d. All surface to be coated shall be completely dry, free of moisture, soil, dust and grit at the time of coating.

Preparation of Coating

- a. The coating specified for this work is a two-component system containing all of the resin in one container and the catalyst in a second container.
- b. The material shall be prepared for application in accordance with the manufacturer's insert sheet in the container.
- c. For application in winter time, the handling of the material will be facilitated by storing it in a place where it will be kept at a temperature as high as 65°F or 70°F. The material applies much more readily at these temperatures.
- d. For application in summer time, the material should be stored in some place where it is in the shade. Material in the sunlight will increase in temperature substantially above atmospheric temperatures. If the material in the field is kept under a shelter out of the sunlight, the temperature of the material will not go above the air temperature.

Application of Coating

- a. The coal-tar epoxy shall be applied by spray, either by using a barrel pump of at least 8 to 1 ratio and a heavy duty spray gun similar or equal to Binks 7-E-2, or by use of airless spray equipment of at least 28 to 1 pump ratio. The use of airless spray is preferred and recommended since pinholing is reduced and touchup is practically eliminated.
- b. This is a thermo-setting material. All material catalyzed at any one time must be applied within the time limits

specified in the manufacturer's brochure.

Thinning

a. Whenever possible, the coal-tar epoxy coating should be applied without thinning. Note that this is a thixotropic material which is quite viscous when first opened but which is reduced to spraying consistency by vigorous mechanical agitation for at least five minutes. If thinning must be done, it must be limited to a quantity of thinner not to exceed the equivalent of the catalyst. Only the thinner recommended by the manufacturer shall be used.

Coating Thickness

- a. A minimum thickness of 10-15 mils (0.010-0.015 inches) dry film is required for the coating on all surfaces.
- b. Dry film thickness will be measured by either an Elcometer dry film meter, MIKROTEST dry film thickness gauge, or equivalent.

Inspection

- a. Satisfactory performance will be based upon acceptance of the completed work by the Engineer's Inspector. Each day's work will be inspected by the Engineer not later than the day following application of the coating. The grit-blasting and surface preparation, however, is to be approved by the Inspector before the start of the coating application.
- b. Inspection of the completed work shall be by use of the magnetic film thickness detectors and by visual inspection for pinholing and holidays. The Inspector may also inspect for these defects by means of a low-voltage volt holiday detector. High-voltage detectors (above 100 volts) will not be used. Detection of inadequately coated areas will be indicated by the Inspector by circling with chalk the areas to be touched up. If five or more such deficiencies are found in a 100 sq.ft. area, the Inspector may require recoating of the entire area in which these occur.

Appearance of Finished Coating

- a. The finished coating shall be generally smooth, glossy, and free of protuberances which could be removed by abrasion. A minor amount of sags, dimpling and curtaining which does not exceed 2% to 3% of the surface will not be considered cause for rejection unless they present sharp edges which might cause removal from abrasive reaction.
- b. In the event the Inspector directs removal of sharp protuberances, they shall be cut off using a sharp wood chisel laid flat against the surface. The zones from which material is removed shall be lightly wire-brushed and wiped with methyl-Isobutyl-Ketone and recoated to smooth the surface.

(b) Butadiene-Styrene. Thin-film coatings of butadiene-styrene and related copolymers are available, providing excellent resistance to many corrosives. These coatings provide excellent bonding, used without primers. Some use with oil primers is also found. Available as either solution or emulsion, butadiene-styrene coatings provide good protection in mildly corrosive applications.

A typical composition for this type coating is 35 to 45% solids, 60 to 80% of which are styrene resin.

(c) Vinyl Resin. Vinyl-based thin-film coatings are used for pipe from 3/4" to 12". They resist acid, alkali and other chemical attack, although solvent-attack is sometimes a problem. Tough and impact-resistant, vinyl thin films also exhibit strong bonding ability.

The basic vinyl resin can be altered to produce many variations. Currently, "hot milling" (mixing with application of heat and high pressures) produces the most satisfactory material for coating. Electrostatic-spraying, the best means of application, requires this vigorous mixing technique for proper application of vinyl.

Vinyl is applied to pipe as follows: Bare pipe is heated to remove moisture and then grit-blasted to clean metal surface. Buffing followed by priming with compatible primer is next. Pipe is then heated to from 460° to 580°F for coating. Charged vinyl powder finely divided by grinding is electrostatically sprayed from a fluidized bed. Infrared heat completes the coating process, followed by water quench to room temperature. Coating thickness is generally 12 to 15 mils.

(8) Waxes. Microcrystalline wax based coatings are similar in application to hot tar coatings. (For reference see NACE 2L161 "Hot-Applied Wax Type Protective Coatings and Wrappers for Underground Pipelines".) Required thickness is generally about 40 mils, however, applied without primer but with a thin plastic wrapper for mechanical strength. Temperature limits are lower for wax coatings than for hot tar coatings. Because of this and other limitations, wax coatings are not in general use.

(9) Cold-Applied Mastics. Cold-applied mastics are sometimes used when it is not feasible to use hot-applied coatings. These are usually manufactured from coal- or asphaltic-tar cutbacks. Curing and hardening occurs through evaporation of the solvent. Reinforcing wrappers are generally included; optimum coating thickness is obtained with several coats (20 to 40 mils). Sometimes a chemical curing step is included; this limits the "pot life", requiring rapid application of mixed coating.

Cold-applied mastics are not in general use for underground structures. In general, their effective life underground is approximately five years and they are limited in

temperature range. Also, these coatings are often soluble in common solvents, because lighter ends are included from the coal-tar or asphalt base. Although these coatings are not generally recommended for underground use, they do provide some protection and may often be used when costs or temperature requirements disallow hot-applied coatings.

5.4.2 Wrappers. Wrappers are employed for several reasons, and serve in one or more ways:

As an outer barrier to prevent and/or indicate coating damage during handling, transit, storage, and installation,

to reflect heat that could soften and deform coating,

to provide reinforcement within coatings, improving mechanical properties,

as a shield between coated structures and backfill, helping to prevent holidays in service,

to improve dielectric properties of coating,

as coating systems in themselves (as tapes or sleeves).

The particular coating and structure situation determines wrapper selection. Some wrappers and uses are discussed here.

5.4.2.1 Pipeline Felts. Pipeline felts are outer wraps, usually of glass fiber or asbestos. They serve as protective layers for enamel or other coatings. (For reference see AWWA Specification C-203-62; Mil. F-18999A (3/10/64).) Usually bonded to the coating, pipeline felts are saturated with coal tar or asphalt, depending on coating composition. These wraps are sometimes used over thin film or tape coatings and may have a reflecting surface.

Rag felts made from fabric have been used as outer wrap. These are not generally recommended. They consist of organic material which may rot in the environment, exposing coating or producing conditions favorable for bacterial corrosion. Non-rotting asbestos or alkaline-resistant glass fiber wrappers should give better service. In alkaline soils or where cathodic protection is applied (producing alkaline conditions), sodium glass and other non-resistant glasses may dissolve.

Pipeline wrappers are commonly available in two weights: 8 or 15 lbs/100 ft² (see Table 5-10 for standard roll sizes and coverage data). Often, they have a reflecting surface, such as sulfate kraft paper, to prevent heat absorption.

Table 5-10a

Typical Widths, Lengths of Pipeline Felt Rolls

Standard Roll Widths (inches) 2, 2-1/2, 2-3/4, 3, 4, 5, 6, 6-1/2, 8, 9, 10, 12, 16, 18 and 36.
 Standard Roll Lengths (feet) 100, 150, 400, 600, 800, 1000, 1200, 1500, 2200, 3800.

Table 5-10b

Typical Coverage and Overlap for Pipeline Felt

Pipe Size (inches)		Bare Pipe Surface Area per Mile (sq.ft.)	Lap (Inches)	Width of Wrap (Inches)	*Squares of Wrap Required per	
Nominal	OD				Mile	1000 Lin.Ft.
1	1.315	1817	1/2	4	24	4.6
1-1/2	1.900	2625	1/2	4	33	6.3
2	2.375	3280	1/2	4	41	7.7
2-1/2	2.875	3980	1/2	4	49	9.2
3	3.500	4838	1/2	6	56	10.6
3-1/2	4.000	5528	1/2	6	64	12.0
4	4.500	6220	1/2	6	71	13.5
4-1/2	5.000	6911	1/2	6	79	14.9
5	5.563	7689	1/2	6	87	16.5
6	6.625	9158	3/4	9	103	19.5
8	8.625	11922	3/4	9	133	25.2
10	10.750	14860	3/4	12	162	30.6
12	12.750	17624	1	12	195	36.9
--	14	19352	1	18	208	39.4
--	16	22117	1	18	237	44.9
--	18	24881	1-1/2	18	273	51.7
--	20	27646	1-1/2	18	303	57.4
--	22	30411	1-1/2	18	332	63.1
--	24	33175	1-1/2	18	363	68.7
--	26	35940	1-1/2	18	393	74.4
--	28	38704	1-1/2	18	423	80.1
--	30	41469	1-1/2	18	453	85.8
--	36	49763	1-1/2	18	543	102.8

* All quantities of wrap are estimated over coated pipe allowing for 1/8" coating thickness. No allowance has been made for waste. For machine application, allow 3% to 5% additional for waste, patching, etc. For hand wrapping, double the amount of lap.

5.4.2.2 Reinforcing Wrapper. Wrappers (impregnated or non-impregnated) are also used for reinforcing enamel coatings. (For reference see AWWA Specification C-203-62; Federal HH-C-466B.) Used between two layers of enamel, they are applied to increase coating strength and prevent cold flow. Open weave glass wrappers are often pulled into the enamel so only one heavy coat is required. These may also be used with cold-applied coatings.

Reinforcing wrappers should be surrounded by coating and not in contact with the structure, to be fully effective. As with outer wraps, reinforcing wrappers of fabric or soft glass should be avoided. Rag fibers protruding from coating can absorb moisture, waterlogging the entire reinforcing wrapper. This is especially damaging at points of structure-to-wrapper contact.

Reinforcing wrappers are available in rolls of standard widths and lengths.

5.4.2.3 Rockshield. Rockshield is a supplemental outer wrap used to protect pipe in rocky ground. This may eliminate dirt or sand trench padding, by cushioning pipe during installation and service. It is tar-impregnated fiber board, available in slabs 1/8" to 1/4" thick. (See Table 5-11 for standard slab dimensions and coverage data.)

It is usually strapped or taped in place circumferentially, and does not exhibit a uniform bond to the structure. Water can become trapped beneath it. (Sometimes, however, it is "sealed down" with hot enamel to prevent slippage.) Therefore, rockshield should be used only with well-coated lines. Another application is padding under river clamps, weights and hold-down anchors.

5.4.2.4 Loose Polyethylene Sleeves. Loose fitting, unbonded polyethylene in sheet or tube form has been used recently as a wrapper for buried, uncoated cast-iron pipe. It is installed by either of the following two procedures:

(1) Polyethylene sheet, formed into tubes of considerably larger diameter than the pipe, is cut to the length of individual pipe sections, placed around them, and sealed with tape.

(2) Sheet polyethylene, cut to fit a pipe section, is wrapped, overlapped, and secured circumferentially by tape.

This coating does not provide complete sealing of metal from ground water or air and is not designed to prevent seepage. However, foreign material is kept from directly contacting the metal structure.

Table 5-11

Typical Widths, Lengths of Rockshield Slabs
 Standard Widths (Inches) 17 to 72
 Standard Lengths (Inches) 36 to 120

Nominal Pipe Diameter (Inches)	Actual Pipe Diameter (Inches)	Recommended			Squares Required per	
		Thickness (Inches)	Width (Inches)	Length (Feet)	1000 Ft. of Pipe	Miles of Pipe
2	2.375	1/8	12	8-0	10.0	53
2-1/2	2.875	1/8	12	8-0	10.0	53
3	3.500	1/8	15	8-0	12.5	66
3-1/2	4.000	1/8	15	8-0	12.5	66
4	4.500	3/16	17	8-0	14.2	75
4-1/2	5.000	3/16	18	8-0	15.0	79
5	5.563	3/16	20	8-0	16.7	88
6	6.625	3/16	24	8-0	20.0	106
7	7.625	3/16	27	8-0	22.5	119
8	8.625	3/16	30	8-0	25.0	132
9	9.625	3/16	34	8-0	28.3	149
10	10.750	3/16	36	8-0	30.0	159
11	11.750	3/16	40	10-0	33.3	176
12	12.750	3/16	44	10-0	36.7	194
13	14.000	3/16	48	10-0	40.0	211
14	15.000	3/16	51	10-0	42.5	224
16	16.000	3/16	54	10-0	45.2	239
18	18.000	3/16	60	10-0	50.0	265
20	20.000	3/16	66	10-0	55.0	290
22	22.000	3/16	72	10-0	60.0	317
24	24.000	3/16	72	6-8	66.7	352
26	26.000	3/16	72	7-2	71.6	378
28	28.000	3/16	72	7-8	76.6	404
30	30.000	3/16	72	8-2	81.6	431
32	32.000	3/16	72	8-8	86.5	456
34	34.000	3/16	72	9-2	91.6	484
36	36.000	3/16	72	10-0	100.0	528

A study of polyethylene wrappers was made by The Cast Iron Pipe Research Association (reference 15), with some good results reported. One theory advanced for this is that oxygen, in the presence of ground moisture under polyethylene, is depleted during an initial corrosion reaction at the surface of cast iron. Once this oxygen is used, no more is available, and no further corrosion can occur.

While it is true that, even for steel, depletion of oxygen will prevent some types of corrosion; other types of corrosion (that caused by anaerobic sulfate-reducing bacteria in particular) will accelerate in the absence of oxygen. Also, the reported effectiveness is at least partially because products of corrosion of cast iron are retained by the free graphite constituent of pipe to form a barrier. Corrosion products of steel will not adhere in this manner.

The effectiveness of loose fitting, polyethylene pipe sleeves is at best debatable. By requiring bonded coatings and cathodic protection for pipes transporting hazardous liquids or natural gas, the Department of Transportation in effect prohibits using loose sleeves for such applications. (Cathodic protection - assuming remote anodes - cannot be applied beneath unbonded coatings.)

5.4.2.5 Loose Polyethylene Wrappers for Tanks. Loose fitting polyethylene wrappers have been suggested for use as total corrosion protection for buried steel tanks. The soundness of this application is questionable. The same problems associated with loose fitting pipe sleeves apply to tanks. In addition, corrosion products of steel are not retained as they are in cast iron. Consequently, when corrosion occurs, failure is often more imminent than with cast iron.

5.4.2.6 Tape Coatings. Several types tape are used for full coating systems. Some are hot-applied; others, cold-applied. As with any coating, hot-applied tapes when properly applied to clean, dry metal serve better underground. Cold-applied systems generally achieve no more than a five-year life or so underground. As with non-tape cold-applied coatings, cold-applied tape may be specified when hot-applied coatings are not feasible for mechanical and economical reasons.

a. Hot-Applied. Several hot-applied tape coatings are used. (For reference see Federal Specification HH-T-30a.) These are basically similar, consisting of organic or inorganic fibers impregnated and thoroughly coated with coal-tar pitch. Plastic film is embedded into this as both separator and outer wrap. These coatings are best applied over primer compatible to coal-tar pitch. Tape coatings using organic (cloth) fibers are easier to apply but

generally inferior to those using inorganic (usually glass) fibers. Organic matter can rot, providing an environment which can support bacterial corrosion.

Specifications for a typical hot-applied tape are given here.

Tape Coating (Hot-Applied)

Tape-form hot-applied coal-tar coating system shall consist of one coat of coal-tar primer, and a single layer of tape. Primer shall be compatible with the coal-tar tape coating and shall be cold-applied to clean dry surfaces. The coating tape shall consist of a plastic film embedded in pliable coal-tar coating, bonded and impregnated into high-tensile strength fiber glass fabric base completely saturated with coal-tar pitch. Coal-tar coating shall have the following general properties:

Softening Point	170°F-175°F (ASTM E-28)
Penetration at 77°F	8 (ASTM D-5)
Thickness	58 mils \pm 2
Dielectric Strength	12 KV (Exceeds)
Salt Crock Test	Passes (ASTM G-8 Cathodic Disbonding)
Meets Federal Specification	HHT 30a
Meets AWWA Specification	C203-71
Compatible with coal tar, asphalt, polyethylene, polypropylene and epoxy mill or yard coating.	

Application shall be either spiral or cigarette wrap. For the spiral wrap after initial priming, the torch flame shall be flashed on coating side of tape (not film side if tape has plastic film). Coating side shall be applied to surface, alternately heating and then spirally wrapping in single thickness with 1/2" minimum overlap of tape. Any plastic film must be flashed off the overlapped area. For the cigarette wrap after initial priming, strips of tape shall be cut to circumference of pipe plus 2 inches and applied to pipe circumferentially, heating as above.

Manufacturer's specifications, for the particular tape used, should be consulted. It is also advisable to have manufacturer's field representative to instruct application crews and periodically monitor the work.

b. Cold-Applied. Cold-applied tapes of many kinds are used, generally only where hot-applied tapes are infeasible. Some are used without primers, although in general this improves metal-to-coating bond. Uses other than complete coating systems are:

Coating welded joints,

Small jobs where economics make use of equipment for hot-applying infeasible,

Patching damaged sections of mill-wrapped pipe for

installation,

Patching for repairs to excavated lines.

One type consists of a coal-tar material or coal-tar-resin compound bonded to a plastic outer film, applied over a coal-tar base primer. Other tapes used are made from plastics (usually polyvinylchloride or polyethylene), applied to primed surfaces. These may be adhesive, rubber-backed, or used in combination with microcrystalline wax. Paper outer wraps may be added.

Cold-applied tapes are frequently less costly than other underground coating systems; they require less equipment and fewer trained personnel for installation. However, their relatively short in-service life (about five years) limits their use.

5.4.2.7 Other Wrappers. Dielectric wrappers made of various thin-film plastics (acetate, polyester, mylar) are sometimes used to improve a coating's electrical strength. These may be bonded to a reinforcing mat or fabric to provide improved mechanical and electrical properties. Dielectric wrappers are often used over microcrystalline wax or grease-based coatings.

5.5 INHIBITORS. From a corrosion standpoint, an inhibitor is a substance which, when added to the environment in proper amount, eliminates or sharply reduces corrosion. Inhibitors are especially important in water, steam, and condensate lines, although they are used in many other environments.

Inhibitors generally reduce corrosion by polarizing the anode (anodic inhibition) or cathode (cathodic inhibition), or by forming deposit on the metal surface, increasing circuit resistance (general inhibition).

5.5.1 Polarization Diagram. Polarization, discussed in paragraph 3.7, is a change in potential of an electrode because of a current flow. Examination of polarization diagram similar to Figure 3-7 reveals how inhibitors can affect polarization.

Anodic inhibitors increase polarization of the anode (Figure 5-2a), reducing corrosion current (ΔI). This means corrosion is retarded.

Cathodic inhibitors increase polarization of the cathode, also reducing corrosion current (ΔI) (Figure 5-2b). Most inhibitors actually affect both electrodes, one more than the other.

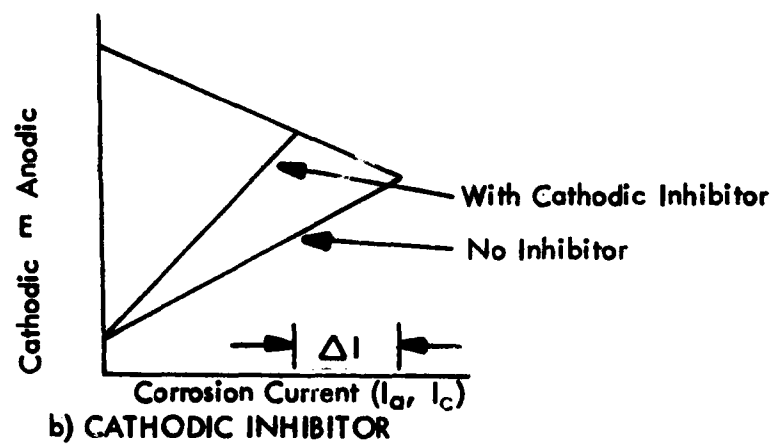
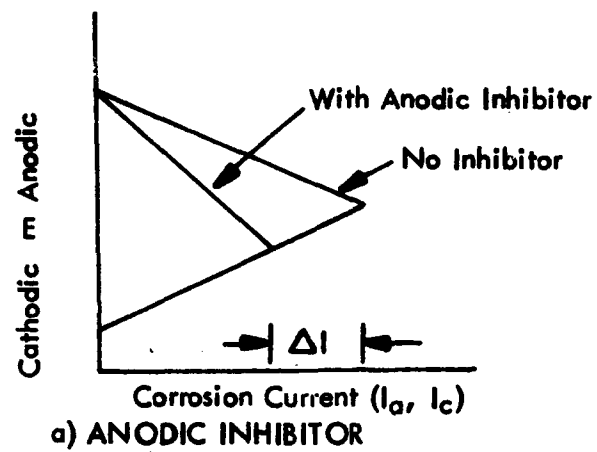


Figure 5-2
EFFECT OF INHIBITORS ON POLARIZATION DIAGRAMS

General inhibitors form a film or deposit on the metal surface, increasing overall circuit resistance. The result is decreased corrosion current, as with other mechanisms.

5.5.2 Types of Inhibitors. In addition to classification by method of polarization (anodic, cathodic, general), some inhibitors are differentiated in other ways. Important types are discussed here.

5.5.2.1 Passivating Inhibitors. Passivation was discussed in paragraph 3.8.1. Environments which passivate steel and other susceptible metals contain anodic inhibitors called passivating inhibitors. The film formed by the inhibitor on active-passive metal is cathodic to bare metal. If this film does not cover the entire surface, corrosion may increase due to the area effect (paragraph 3.2.3.3.a). This can occur if insufficient passivating inhibitor is present.

Examples of passivating inhibitors which affect steel are chromates, nitrates, and nitrite ions (no oxygen present). Others, such as phosphate, require oxygen.

5.5.2.2 Vapor Phase Inhibitors. Vapor phase inhibitors are volatile compounds used in a closed system, which travel as vapor, condensing on the corroding metal. There it forms protective ions (such as nitrites to passivate steel). Compounds such as dicyclohexylamine nitrite and others inhibit corrosion of boiler condenser tubes and closed shipping containers in this manner.

5.5.2.3 Organic Inhibitors. Organic inhibitors are usually classified under "general control", because they affect both anode or cathode to varying degrees. The general mechanism of this class is formation of a surface film, a few molecules to several thousandths of an inch thick. Sulfonates and various amines are commonly used organic inhibitors.

5.5.2.4 Precipitation Inhibitors. Precipitation inhibitors also fall into the "general control" class, in producing precipitate films over the entire metal surface.

Common precipitation inhibitors are phosphates and silicates, used in water. Silicate forms a protective film over steel in aerated, low-salinity water, such as city water supplies. The amount of silicate required, determined by the saturation index, is influenced by water composition and pH.

Phosphates require motion and the presence of calcium and oxygen to be inhibitors. Both phosphates and silicates, being non-toxic, are useful for inhibiting potable water supplies. Chromates or nitrites, more effective inhibitors,

are toxic and cannot be used.

5.6 INSULATION.

5.6.1 General Application. Dielectric material is used to electrically isolate one structure from another. Reasons for this are:

- To separate dissimilar metals, preventing galvanic corrosion,

- To separate structures with different surroundings or different coatings, preventing corrosion due to dissimilar environments,

- To prevent contact between carrier pipes and casing
- To sectionalize one cathodic protection system from another. One system may be in an environment different from that of another section or have a different quality of coating, requiring higher current density for protection, or one section of a pipeline may not require cathodic protection whereas the adjacent section may require protection,

- To prevent cathodic protection current from flowing onto foreign structures,

- To isolate bare electrical cable exposed at splices, connections or other places where current could leave the cable. This also prevents water or other undesirable material from contacting the wire,

- To insulate pipes or cables from concrete or masonry,

- To insulate sections of line from each other to increase total circuit resistance to reduce stray current flow.

The purpose of dielectric insulation is defeated, and insulation is not effective, if low-resistance metallic paths are inadvertently provided around insulation. Dielectric insulation can be "shorted" by metallic hangers or supports connected to steel building beams or other structures. Care must be taken to avoid physical contact between an insulated structure and other buried metallic facilities, including building steel. "Bypassing" with parallel pipes, beams, etc. should be avoided. Insulating material must not be cracked or forced between unaligned fittings. Moisture, mud, etc. must be kept away from insulating material, and any buried insulation must be thoroughly coated before it becomes moisture saturated.

When insulation is used between two different, or sections of the same, underground structures, it never completely (produces infinite resistance) electrically isolates them. This is because the resistance between any two buried surfaces is the sum of their individual surface-to-earth interface resistances. It is not uncommon to install effective dielectric insulators and then measure resistance across

them only to find that it is less than 1.0 ohm. This is effective insulation, however, because corrosion voltages are proportionally small.

Insulation effectiveness can be best determined by testing and inspection both during and after installation. Impressing a voltage across the insulated joint and measuring current flow or resistance indicates insulation effectiveness. A "Megger", or a battery-powered "Vibroground" may be used for this test. The resistance should be infinite when the insulating fitting is tested before its connection to piping. It will usually be much less when buried piping or other metal is connected to either or both sides. A test station with four connections (two on each side of the joint) are required for accurate resistance measurements of buried insulated fittings (paragraph 5.8).

5.6.2 Types.

5.6.2.1 Insulation Through Walls. Insulation is often used on pipes entering building walls to electrically isolate them from the walls themselves or other metallic structures in them. This also prevents the structure from picking up stray currents in the wall which could cause corrosion. Where the line is being cathodically protected underground outside the wall, this insulation minimizes loss of current to other metallic structures through the wall. Figure 5-3 shows an insulation system, for pipe going through a wall. (An air space, rockshield, or pipeline felt might also be inside.) This type insulation is also used around pipe contacting both concrete and soil at various sections (such as radiant heating pipe), to prevent soil-concrete cell corrosion (paragraph 4.3).

5.6.2.2 Insulated Fittings. Insulated fittings are used to electrically isolate one section of a structure from another section of the same structure. Pipe fittings which are commercially available as insulators of dielectrics are:

1. flanges
2. unions
3. couplings
4. nipples

Flanged fittings are insulated with a gasket between flange faces and with sleeves and washers for the flange studs. Asbestos, or reinforced plastics are commonly used for flange gaskets. Mylar or phenolic materials make up washers and sleeves which isolate flange studs. Washers are normally 1/8" thick; sleeves, 1/32" thick. Typical insulated flanges are shown in Figure 5-4.

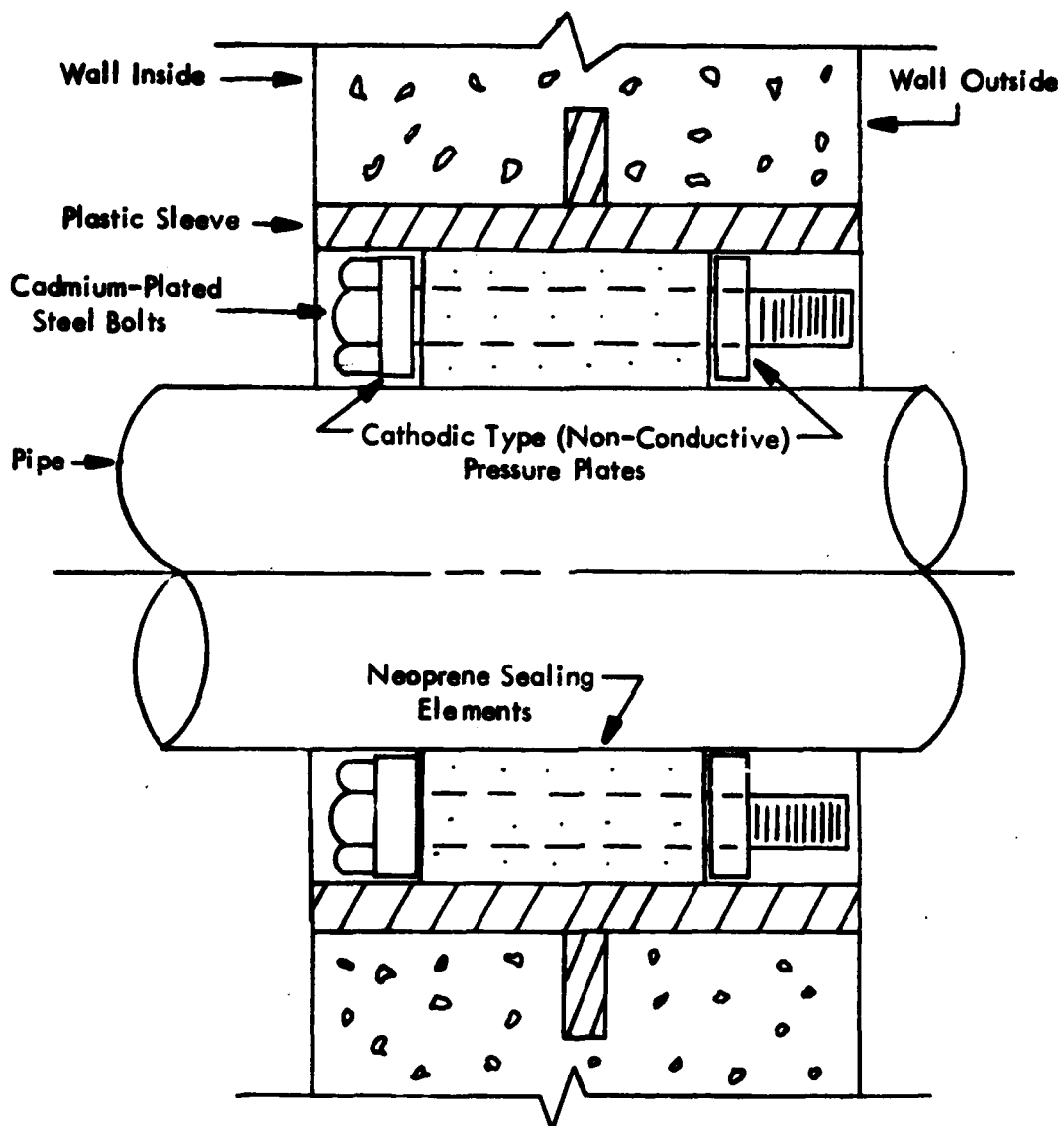


Figure 5-3
TYPICAL INSULATING PIPE SLEEVE ASSEMBLY

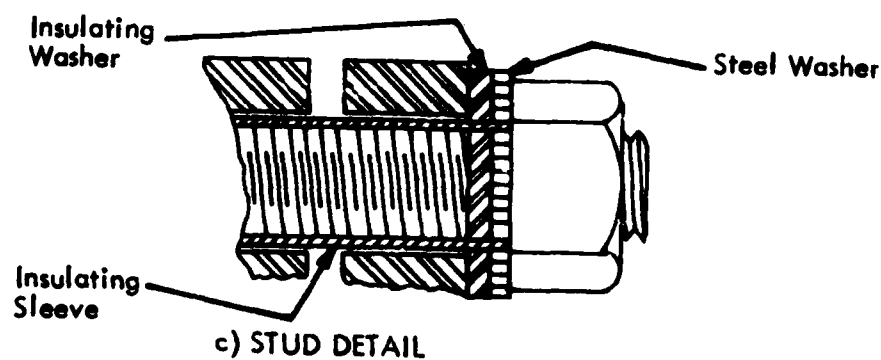
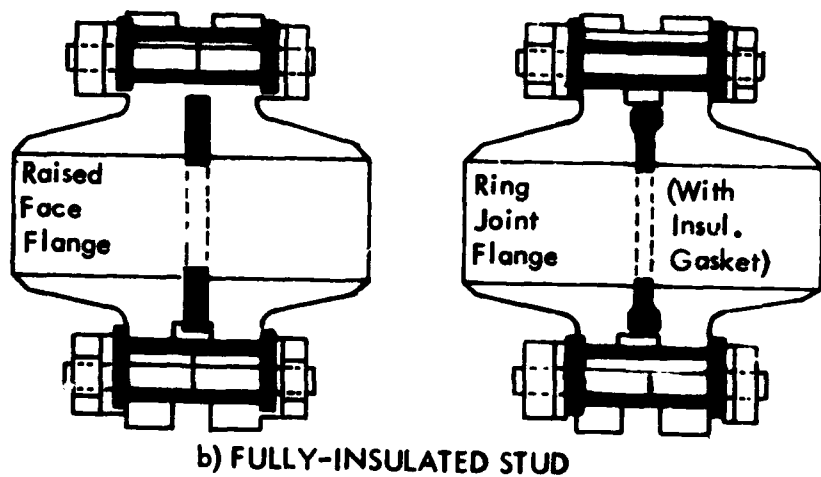
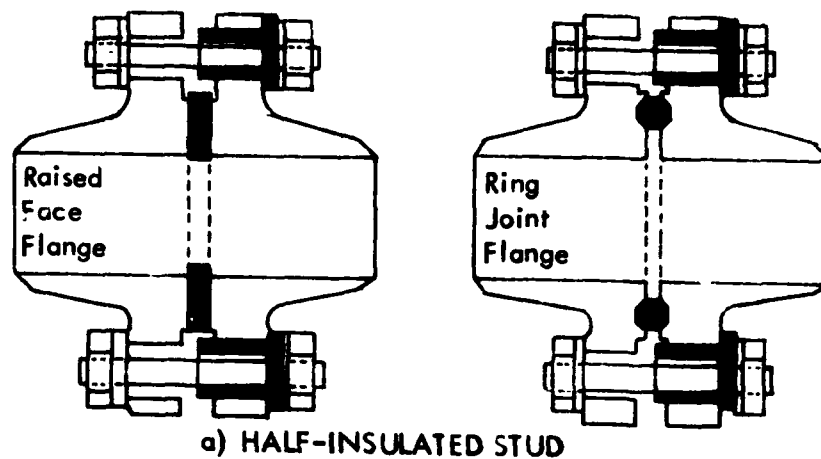


Figure 5-4
FLANGE TYPE INSULATING JOINTS

Screwed fittings commonly insulated are nipples, unions, and couplings. These are used on threaded pipe. Typical examples are shown in Figures 5-5 and 5-6. Although insulated couplings are available as reducers, usually standard couplings supplemented with bushings are used for joining pipe with different size threads.

5.6.2.3 Splice Insulation. Often in corrosion control buried electrical cables require splices; these may be taps at anodes in cathodic protection systems or other underground splices. A typical anode-to-header cable splice is shown in Figure 5-7. After these connections have been made, they must be well-insulated. A field-molded or cast-epoxy resin coating having an insulation value, and resistance to deterioration, equal to or better than the cable insulation is available in kit form.

The plastic mold body is placed over the entire connection. Epoxy resin is activated by squeezing and kneading the package in which it is contained, along with a catalyst, until it is mixed thoroughly. When the color is uniform, the resin is immediately poured. The resin hardens in a few minutes at normal ambient temperatures. These insulated splice kits are designed to be water-tight and insulate the splice as cable insulation does the cable.

5.6.2.4 Casing Insulators and Seals. Casings are sometimes required at road crossings, river crossings and other areas where required by Federal, State, or Local Codes, or actual physical conditions. They consist of larger diameter pipes enclosing the carrier pipes. Their use is discouraged (paragraph 4.15.4). However, casing insulators, cradles and end seals should be installed, and a pipe-to-casing test station should be included (paragraph 5.8.1.3).

Casing insulators (spacers) and cradles are generally plastic: high-density polyethylene or a phenolic material. They electrically isolate the carrier pipe from the metallic casing. They also serve to absorb some of the shock from the road traffic. Sufficient spacers should be used to support the carrier pipe load; the two end units should be located not more than one foot from casing ends, shown in Figure 5-8. Centering cradles may be used in lieu of two spacers located at casing ends if necessary. Cradles have larger runners and serve to center carrier pipe at casing ends to prevent accidental metal-to-metal contact. A typical casing insulator installed on a pipe is shown in Figure 5-9. Casings should always be pumped dry and swabbed before installing carrier pipe.

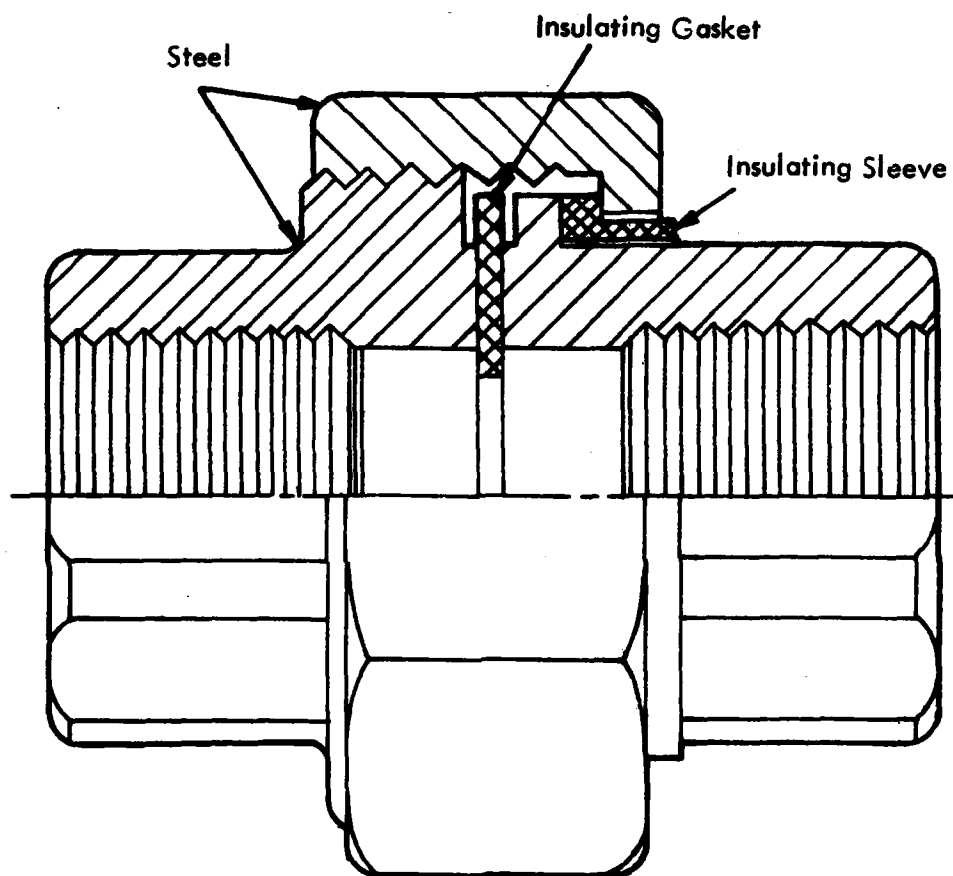


Figure 5-5
INSULATING UNION

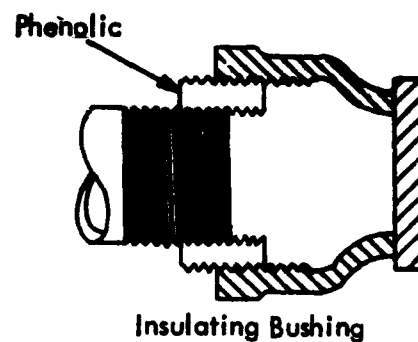
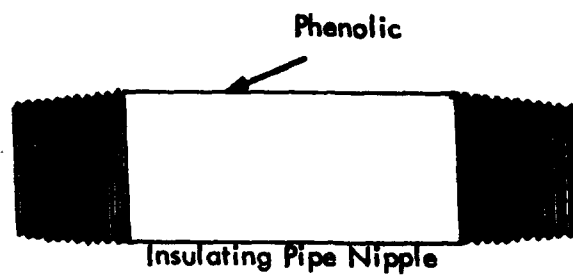


Figure 5-6
INSULATING NIPPLE AND BUSHING

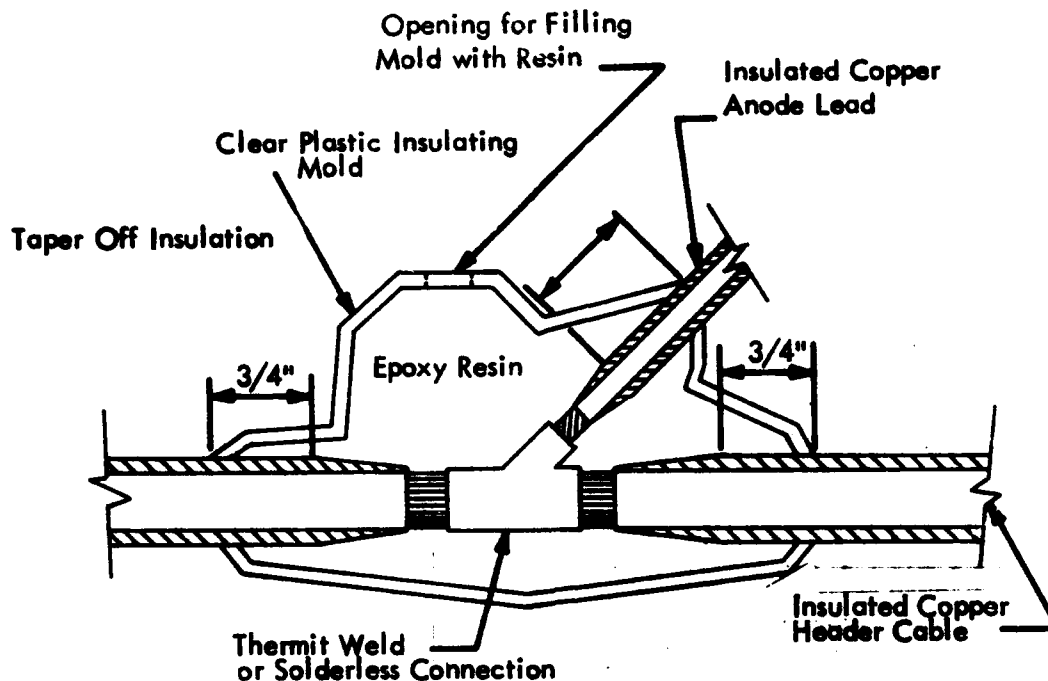


Figure 5-7
EPOXY INSULATED ANODE-TO-HEADER CABLE SPLICE

Flexible molded seals should be installed on ends of casing to exclude water, soil and rubbish from entering casing. Casing ends should be carefully cleaned on the exterior, and two coatings of bituminous primer should be applied before installing end seals to assure a watertight joint.

A typical end seal installed on a pipe is shown in Figure 5-10. Various end seals, insulating spacers, and cradles appear in Figure 5-11.

5.7 BONDING.

5.7.1 Reasons for Bonding. A bond is a metallic connection between two sections of structure or two different structures to carry electrical current. They are used when a voltage exists which will cause current flow from a metal surface to earth, corroding that metal. Bonds are installed as current-carrying bypasses, and, to be effective, the resistance through them must be less than the parallel structure-to-structure resistance.

Bonds are commonly installed across nonconducting (mechanical) pipe fittings, between structures (pipes, tanks, buried cables, building structures, and so on), to allow cathodic protection or stray currents to flow. Sometimes resistors

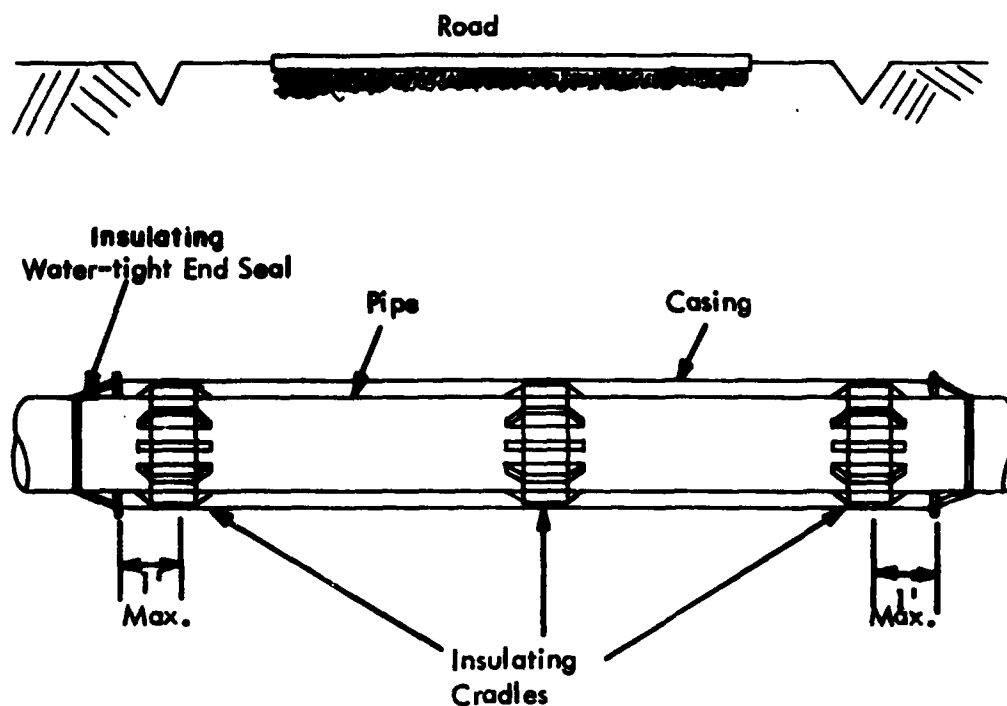


Figure 5-8
ROAD CROSSING CASING

and/or reverse current switches are included with bonds. Bonding often connects dissimilar buried metals together. Unless carefully engineered for the particular condition, these could be detrimental.

Bonds may also be required for safety. For example; where stray or cathodic protection current flows on a buried pipeline containing volatile oil or gases, a temporary bond is needed during repairs. When a section of pipe is cut out with no alternate path for current (such as an adjoining pipeline), sparking can occur. Even if "mud-packing" or other methods of sealing the line are applied, explosive fumes may still be present. A temporary bond, welded to the pipe before cutting into it, can prevent sparking by providing an alternate path for current flow. If the only voltage difference is due to impressed current cathodic protection, another means of preventing sparking is turning off the rectifiers. It is best to establish safety procedures for repair work to determine what precautions are required.



Figure 5-9
SPACER ON LINE .



Figure 5-10
END SEAL

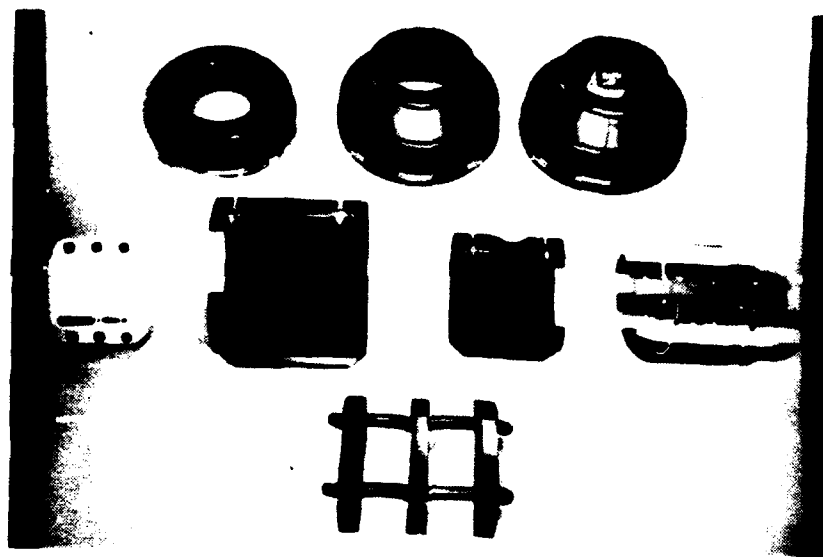


Figure 5-11
VARIOUS END SEALS, SPACERS, AND CRADLES

Temporary bonds may also be needed where ships, airplanes, or trucks are refueled. Underground refueling systems often receive cathodic protection. Stray currents may also be a problem. A potential difference between the underground refueling system and vehicle or plane can cause sparking and explosions. Temporary bonding or rectifier turn-off may be needed. Again, the necessity of safety precautions can be established by measurements, to determine voltage differences.

5.7.2 Method. Bonds between underground structures consist of insulated copper cables, thermit-welded or brazed to structures, to provide paths for cathodic protection current to pass between them. They must be installed across joints in cast-iron pipelines for electrical continuity. On fire protection lines, valves and hydrants must also be bonded. Connections are to be thoroughly coated with coal-tar epoxy or hot coal-tar enamel and pipeline felt so no bare copper is exposed to soil or moisture. If bonds between structures and across joints are not installed properly, cathodic protection current can damage metal.

Typical bond installation for various joints are shown in Figures 5-12 to 5-14. Floating flange and Dresser Coupling-type joints require additional connections to insure electrical continuity of all sections of the joint.

Interference bonds between adjacent structures include a shunt for current measurement and resistor of value calculated to drain just enough current to eliminate stray current corrosion. The resistor and shunt are enclosed in a test box. If resistance value is too high, some corrosive current may still leave the pipe. If resistance is too low and one line is cathodically protected, protective current will be wasted on the foreign line.

Where stray current can reverse direction, as in a multiple-substation electric railway, reverse current switches may be required. Such switches prevent serious corrosion where reversed current discharges to ground. Several switch types are available. The diode type uses a silicon diode with germanium stack to interrupt reverse current. It can, however, rectify stray current. Also, monitoring a diode switch requires expensive equipment. A failed switch becomes open or a solid bond.

Another type switch employs a polarized relay. The relay is self-actuated, operating on the current flowing through it. In order to eliminate flow of large currents through the relay, a current conductor may be added with set voltage limits to open and close it. This type switch is difficult to adjust in the field and requires constant maintenance.

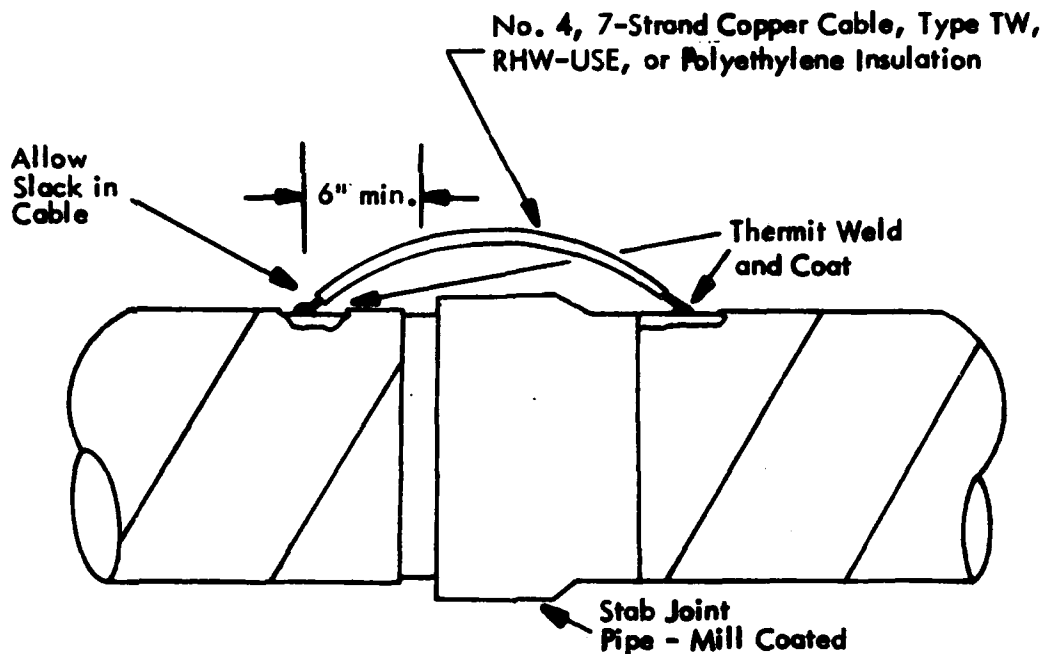


Figure 5-12
STAB JOINT BOND

5.8 TEST STATIONS. Test stations are used at points where the structure or soil is otherwise inaccessible for testing (underground or underwater). They consist of wires attached to the structure and led to a convenient point so that various electrical measurements can be taken after installation. A soil test station (test access hole), which contains no wires, is a means of contacting soil through concrete or asphalt for measuring structure-to-soil potentials.

Test leads connected permanently to a buried structure have these advantages:

1. Time saved in locating line and making connections.
2. Good connections to pipe assured with a minimum of effort.
3. Readings easily repeated at the same location for comparative purposes.
4. Not necessary to break coating when making electrical contact.

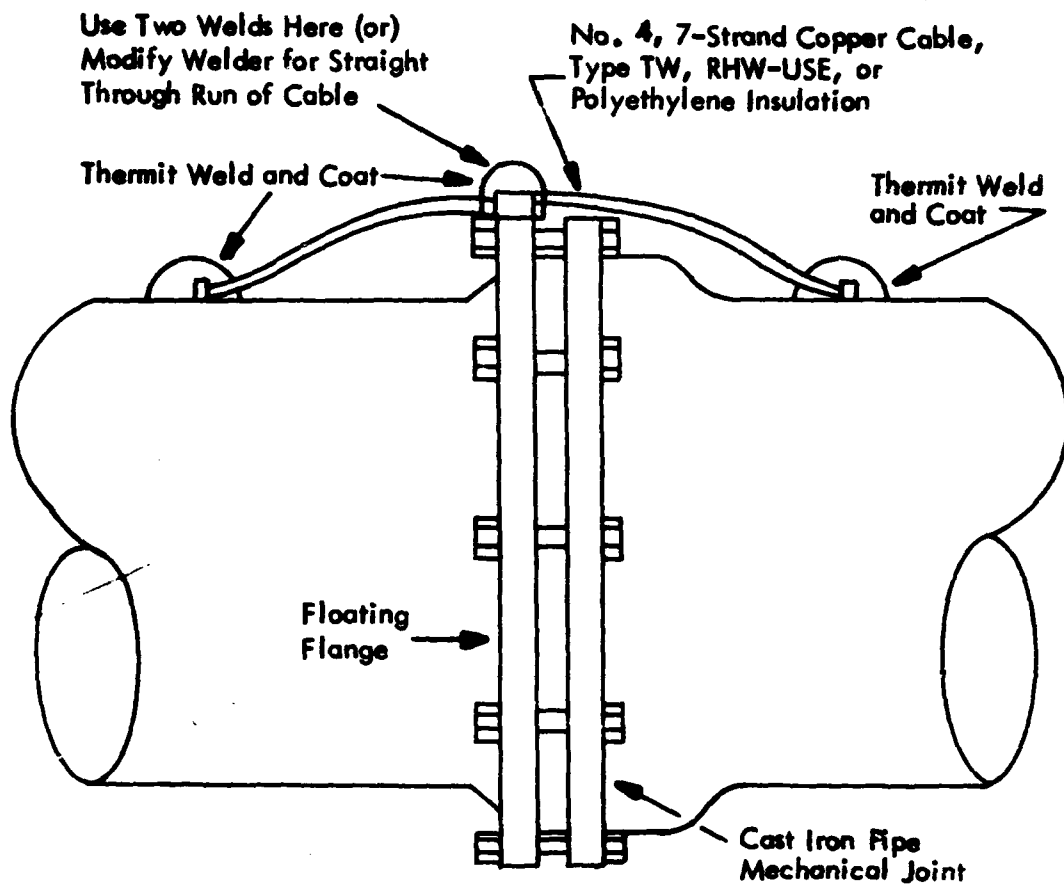


Figure 5-13
MECHANICAL JOINT BOND

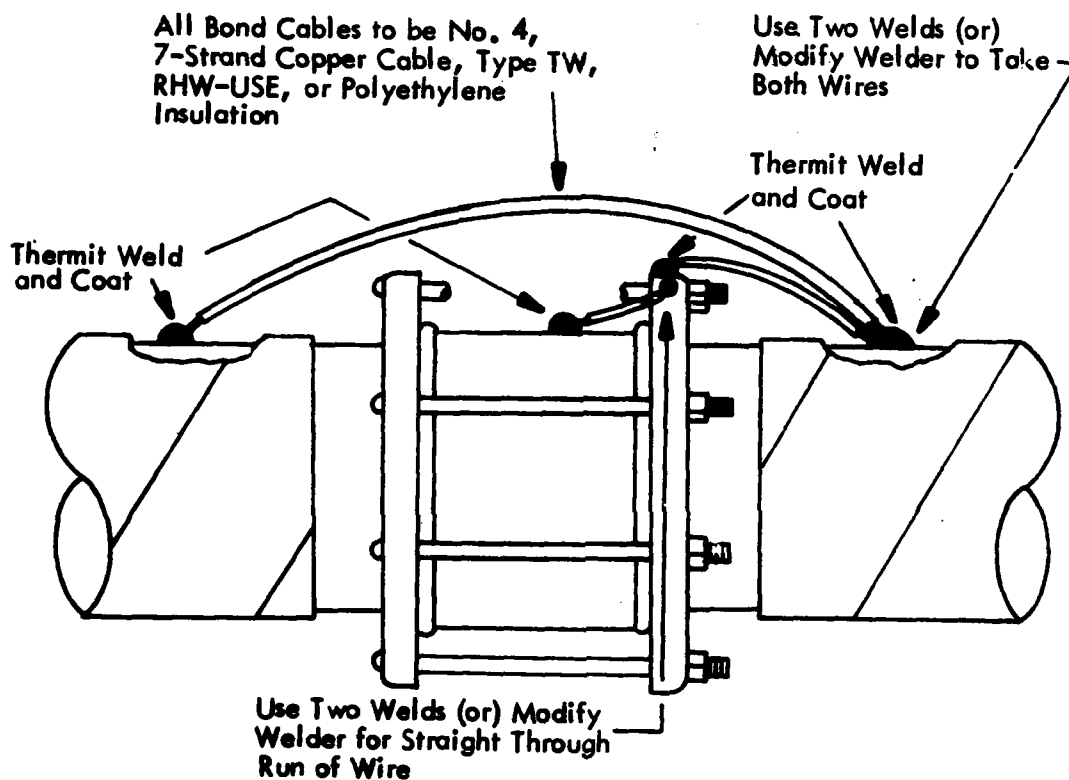


Figure 5-14
DRESSER COUPLING BOND

5. Where a post is used to hold a terminal box for leads, it can also be used as a marker.

Structure test stations consisting of two or more lead wires can be installed on newly-constructed lines and older ones being placed under cathodic protection or subject to stray currents from direct current machinery or cathodic protection applied to foreign structures. The following considerations can determine the location of test installations:

1. Critical points to test effectiveness of applied cathodic protection. (Usually determined by initial surveys.)

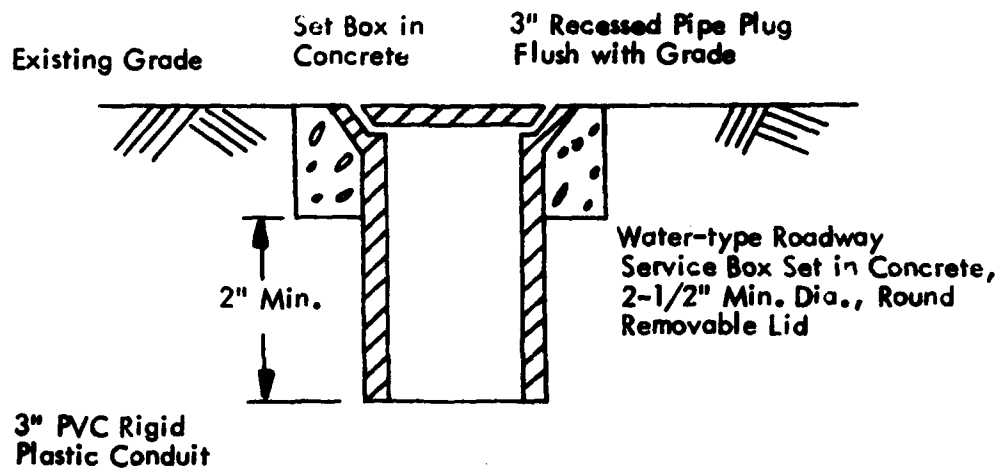
2. Points where an exchange of current has been noted, or is likely to be experienced. (Foreign line crossings, etc.)

3. Points conveniently spaced for the purpose of detecting changes. (Spacing depends upon type of protection employed, number of protection units used per length of line, condition of coating, and density of population.)

Specific types of test stations are described below. Where test leads are included, solid number 12 type TW wire with RHW-USE or HHWPE insulation of suitable color code can be used, thermit - welded to the structure and the weld coated. Stranded No. 12 wire cannot be thermit - welded. Test leads are run from the structure to an easily accessible test box (Figure 5-15). A grade-level test box (Figure 5-15a) is set in concrete or asphalt to prevent settling. An above-grade test box (Figure 5-15b), mounted on a pole or building wall, is threaded into galvanized conduit through which the leads pass. (Above-grade test boxes are preferred.) Inside either type test box, cable ends may be taped to prevent contact, or connected to shunts or a terminal board (Figures 5-16 and 5-17). Shunts are generally used where current measurements are required; a terminal board is for easy connection where a number of leads are present.

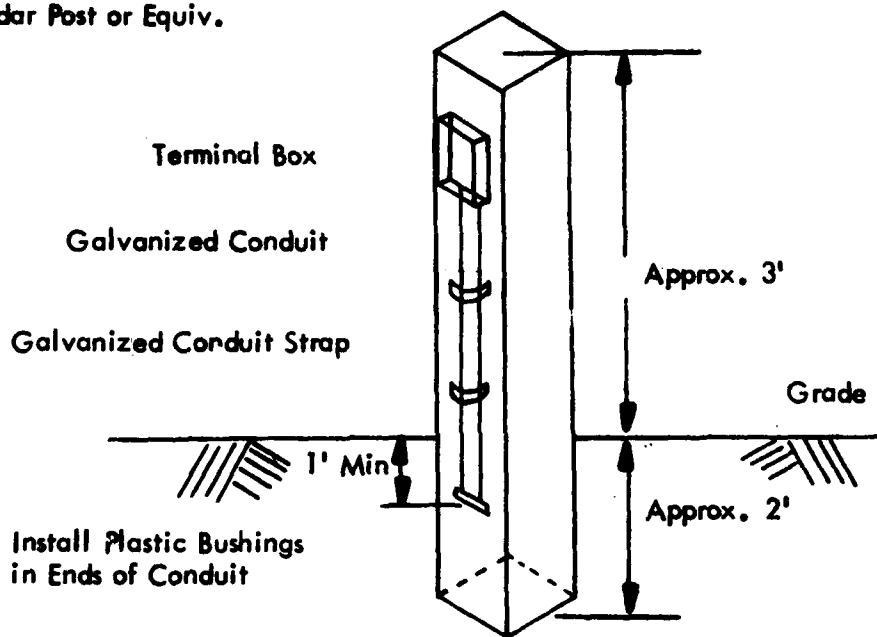
5.8.1 Types of Test Stations.

5.8.1.1 Test Access Hole. A test access hole (Figure 5-18) makes soil beneath asphalt or concrete accessible for structure-to-soil potential measurements. A piece of 3-inch PVC rigid plastic conduit fitted with a 3-inch threaded coupling and pipe plug can be used. The top of each test access hole assembly is installed at the final elevation of finished pavement in that area. The bottom is cleaned out and kept free of stones and debris.



a) GRADE LEVEL TEST BOX

Building Wall or 4"x4" Treated
Cedar Post or Equiv.



b) ABOVE-GRADE TEST BOX

Figure 5-15
TEST BOXES

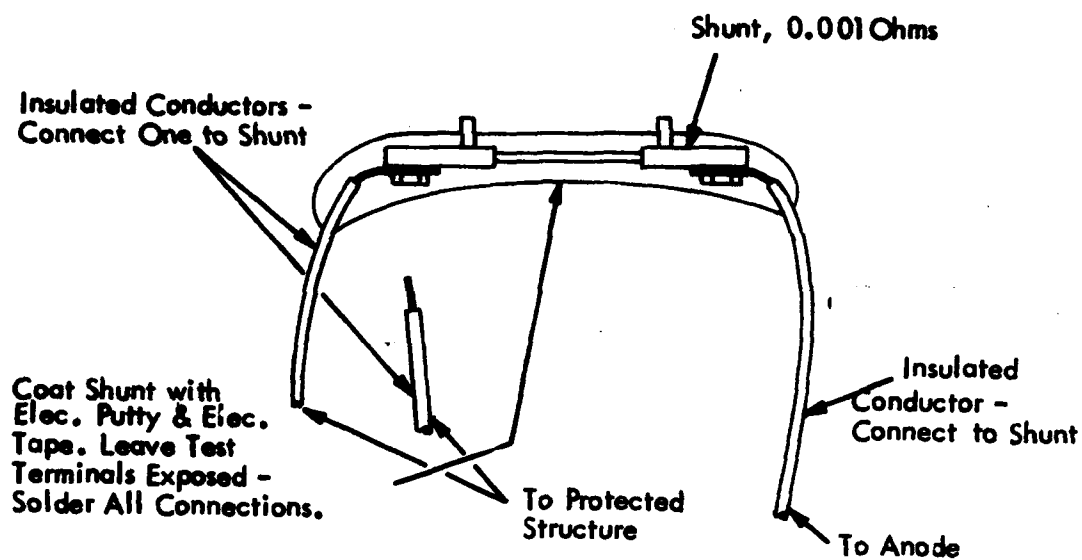


Figure 5-16
SHUNT CONNECTION

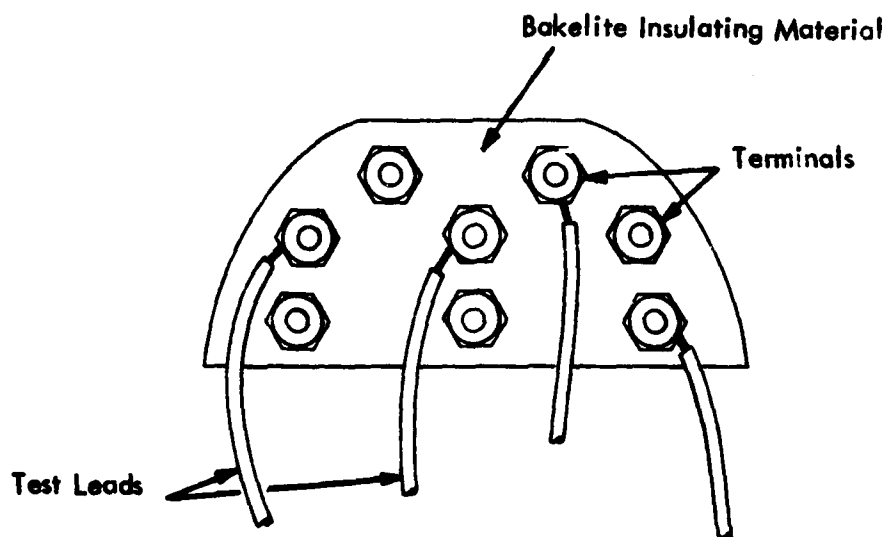


Figure 5-17
TYPICAL TERMINAL BOARD

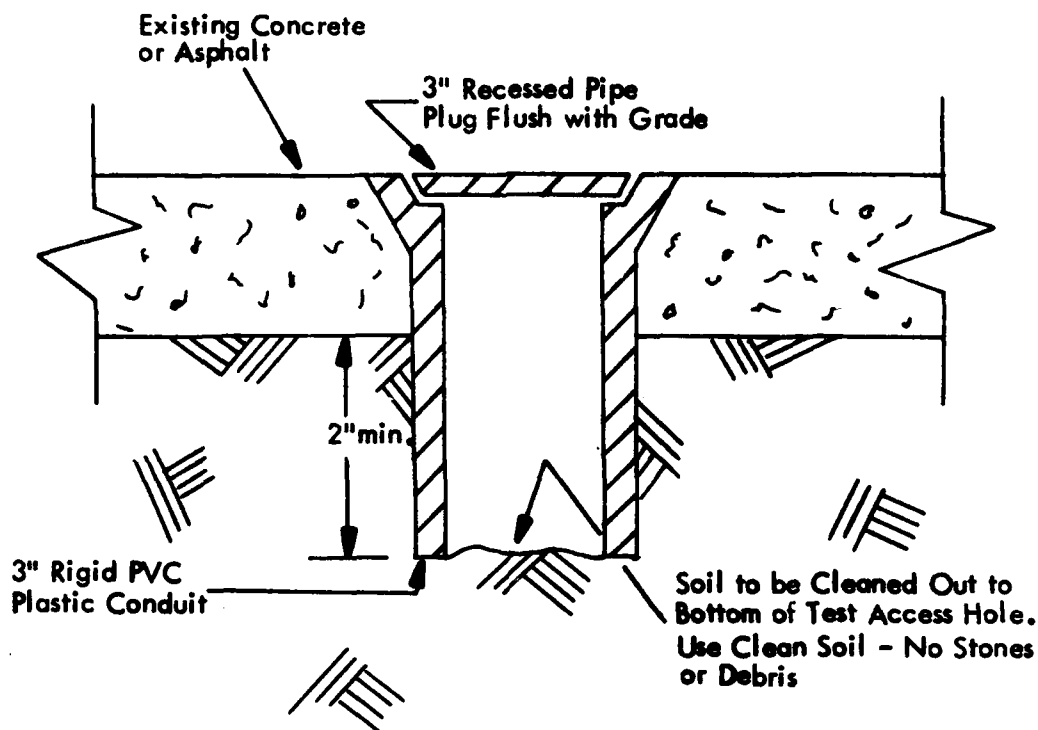


Figure 5-18
CATHODIC PROTECTION TEST ACCESS HOLE

5.8.1.2 Permanent Electrolyte-Contact. Another method of obtaining contact to soil for voltage measurements is a permanent electrolyte-contact station. Electrodes, usually pure zinc in packaged backfill, are installed underground at key points near the structure. Lead wires are terminated in test boxes for use in measuring structure-to-soil potential. Zinc electrodes without backfill may be used with submerged structures. Permanent reference electrodes of the same material as the structure are also used. Attempts to develop copper-copper sulfate electrodes for permanent installation are underway.

Permanently-installed electrodes are of doubtful value. Polarization films can form, and values of electrode-to-earth potentials can become unstable. In general, more accurate potential values can be obtained in inaccessible areas with a test access hole and a standard reference electrode.

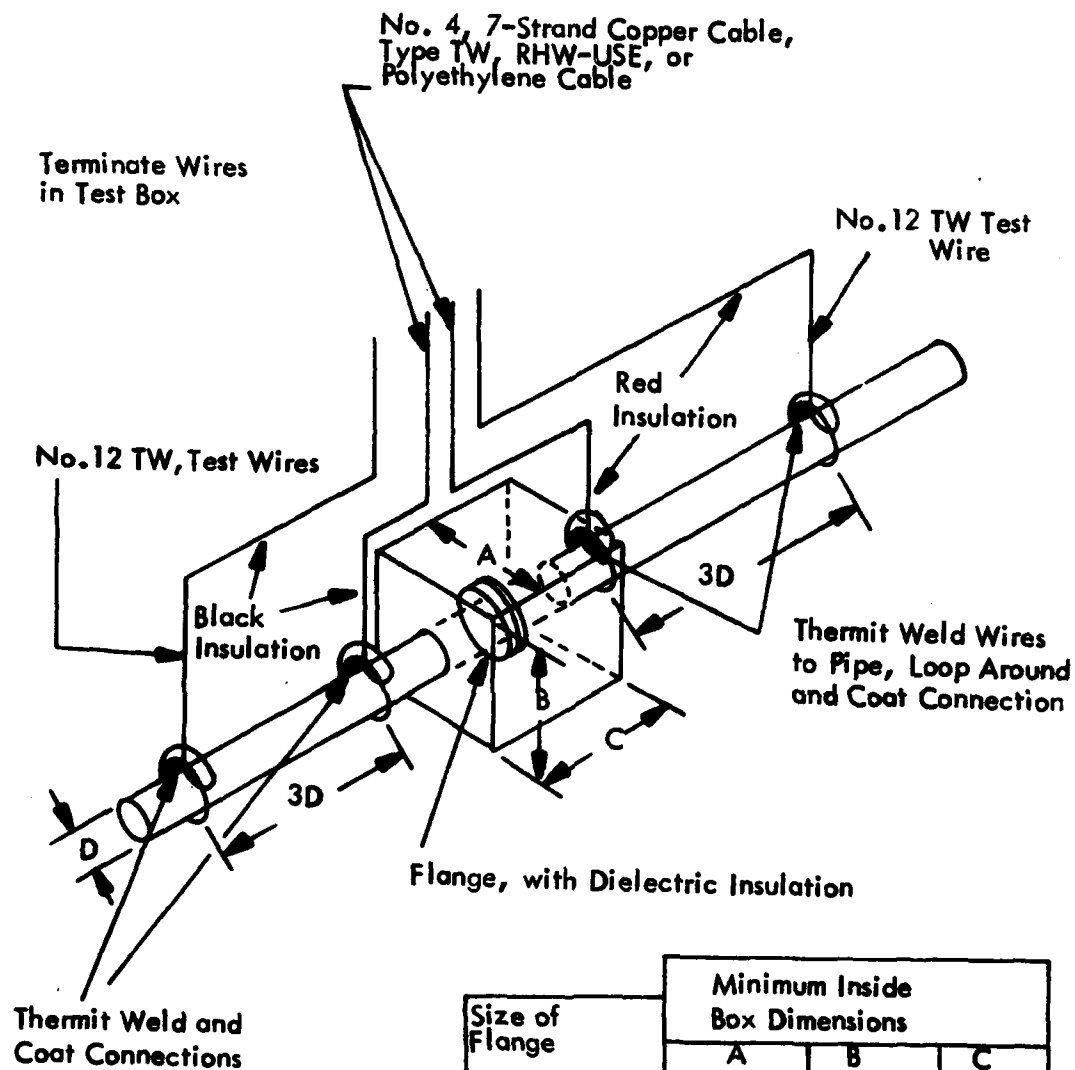
5.8.1.3 Insulation Test Station. Figure 5-19 illustrates test leads installed at an insulated flange. Its effectiveness can be best determined by testing and inspection during and after installation. Impressing a voltage across the insulated joint and measuring current flow or resistance indicates insulation effectiveness. A volt-ohm-milliammeter, a "Megger", or a battery-powered flange tester may be used for this test

Resistance should be infinite when the insulating fitting is tested before connection to piping. It will usually be much less when buried piping or other metal is connected to either or both sides. Two No. 12 test wires are installed, one on each side of the flange. To facilitate installation of a future bond, if required, an extra set of heavier wires (No. 4) are also connected across. These can pass through another test box containing the resistor and an ammeter or the same box. (Although the resistance in No. 12 wire is negligible, heavier wire offers the protection of added mechanical strength.)

5.8.1.4 Hydraulic Cylinder-to-Casing Test Station. The sleeve found around most hydraulic elevator cylinders must be tested for electrical contact to the cylinder and to the building structure. This is important so that proper consideration can be given to using it as an anode in designing cathodic protection. This testing requires installation of test wires as shown in Figure 5-20. Two No. 12 TW test wires are required on each structure in order to obtain accurate resistance measurements. One heavier, No. 4 wire per structure is required in case cylinder and casing become shorted to each other. These two wires are then bonded together to insure electrical continuity for cathodic protection or stray current drainage.

5.8.1.5 Pipe-to-Casing Test Station. As discussed in paragraph 4.15.4, pipe-to-casing resistance affects cathodic protection efficiency. Accurate resistance measurement requires installation of two test leads on each structure, as shown in Figure 5-21. This method eliminates the effects of contact resistance, important because pipe-to-casing resistance may be only a few tenths of an ohm on bare pipe to 2 ohms, or better, on coated pipe. Ohmmeters or circuits employing only one contact to pipe and one to casing should not be used since erroneous readings can result.

5.8.1.6 Foreign Line Crossing Test Station. A test station located where a foreign line crosses a protected line is shown in Figure 5-22. The lines may also be parallel. One No. 12 test lead is attached to each line (with permission from the owner of the foreign line) for making



Size of Flange	Minimum Inside Box Dimensions		
	A	B	C
6" or 8"	24"	See	See
10" or 12"	24"	Note	Note

Note: B & C dimensions must allow a 3" minimum clearance between flange outside diameter and inside box surface.

Figure 5-19

ENAMEL BOX AND TEST POINT FOR UNDERGROUND INSULATING FLANGE

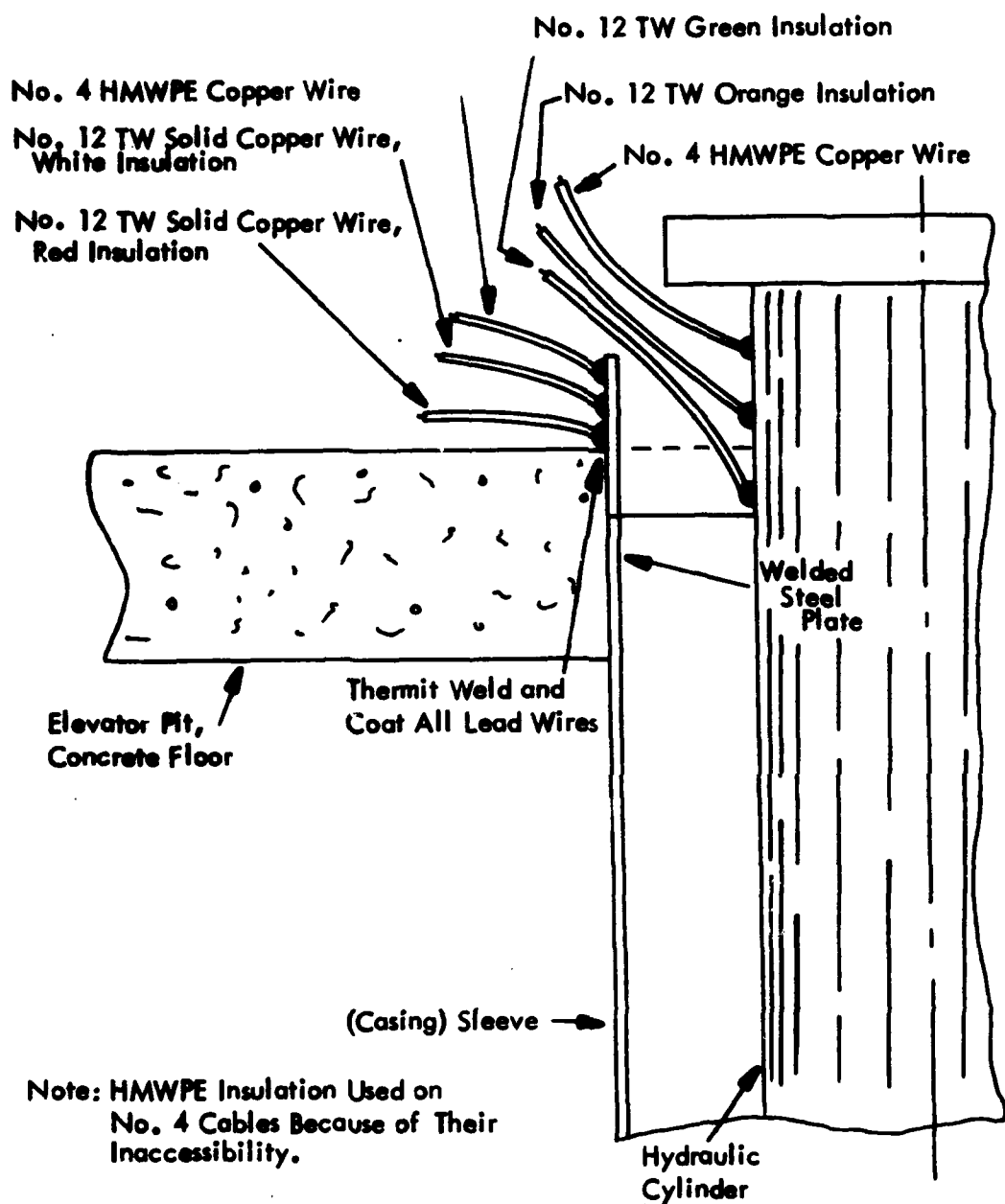


Figure 5-20
HYDRAULIC ELEVATOR TEST WIRE INSTALLATION

Terminate Wires in Test Box

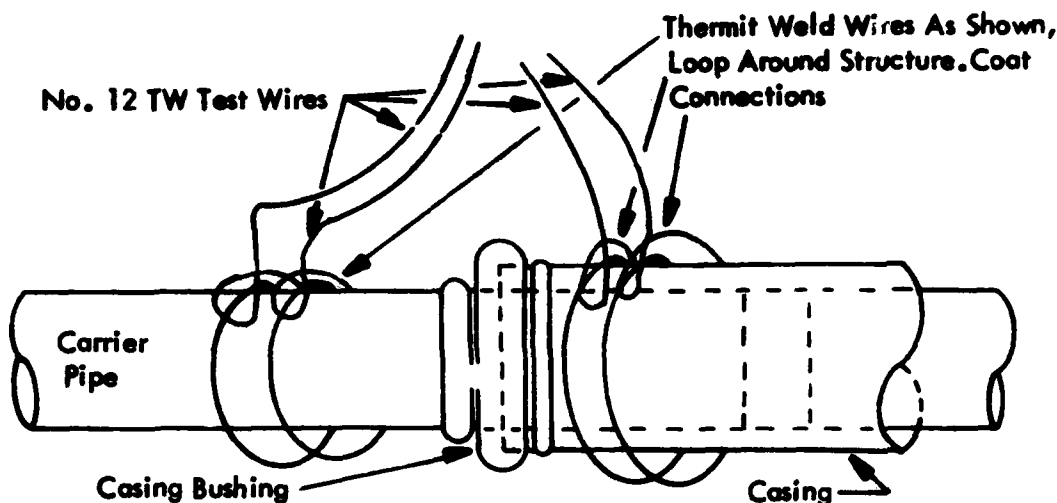
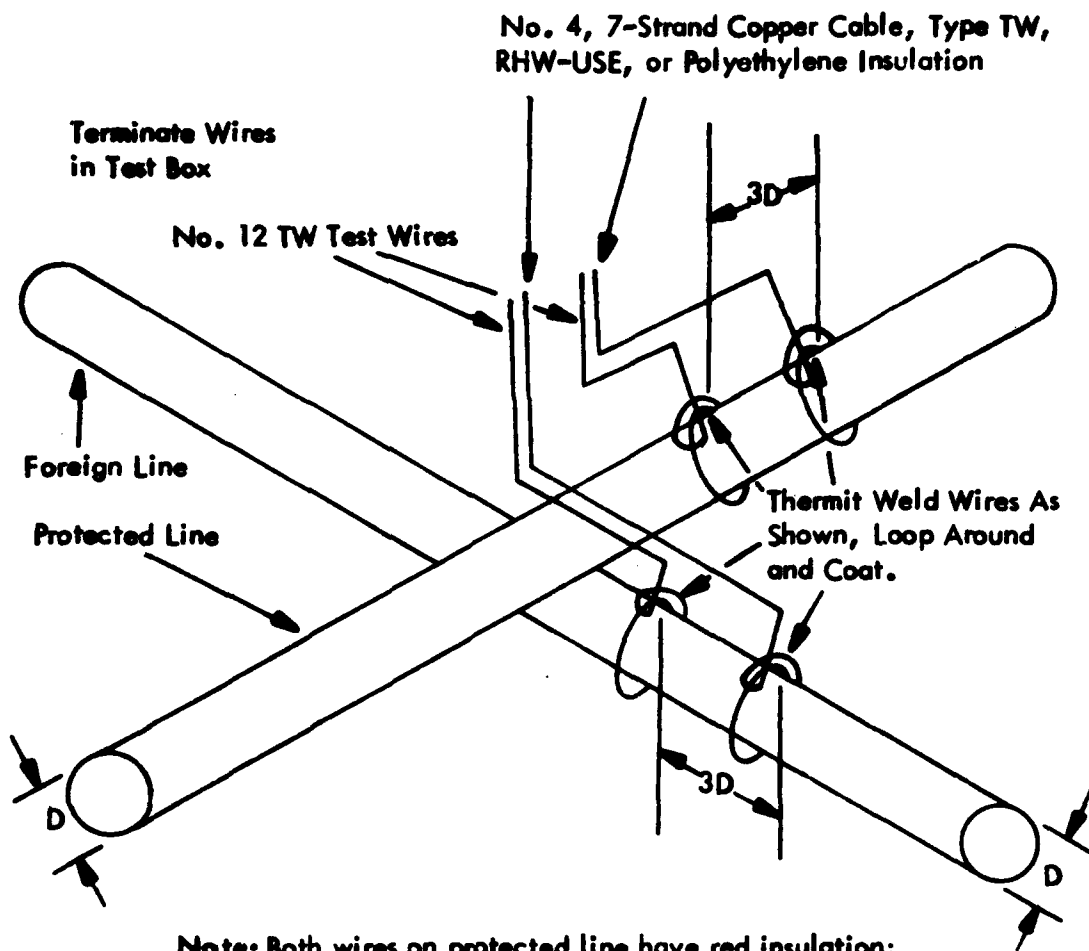


Figure 5-21
PIPE CASING TEST STATION

various measurements such as current flow and direction, voltage difference, and for bond calculations. If current flowing on one structure affects the other, a bond may be required to drain current from the affected structure back to the originating system. The heavier, No. 4 wires, one on each structure, are used for bonding.

5.8.1.7 Anode Test Station. Galvanic anode test stations are often included as part of normal installation to facilitate reading current, structure-to-soil potential, and other electrical measurements. A typical one for a single anode (Figure 5-23) consists of two No. 12 TW test wires thermit-welded to the structure, one of which is soldered at the other end to a copper shorting bar, also connected to the anode lead wire(s), providing a direct connection between anode and structure and an easy means of measuring current. The free ends of the remaining test wire is connected to a separate terminal.

This type test station is normally not required at every anode location in a distributed bed. Where several point beds are used, however, galvanic anode test stations are often included at each connection to structure. Exact placement depends on the specific installation.



Notes: Both wires on protected line have red insulation;
those on foreign line have black insulation.

Figure 5-22
FOREIGN LINE CROSSING TEST STATION

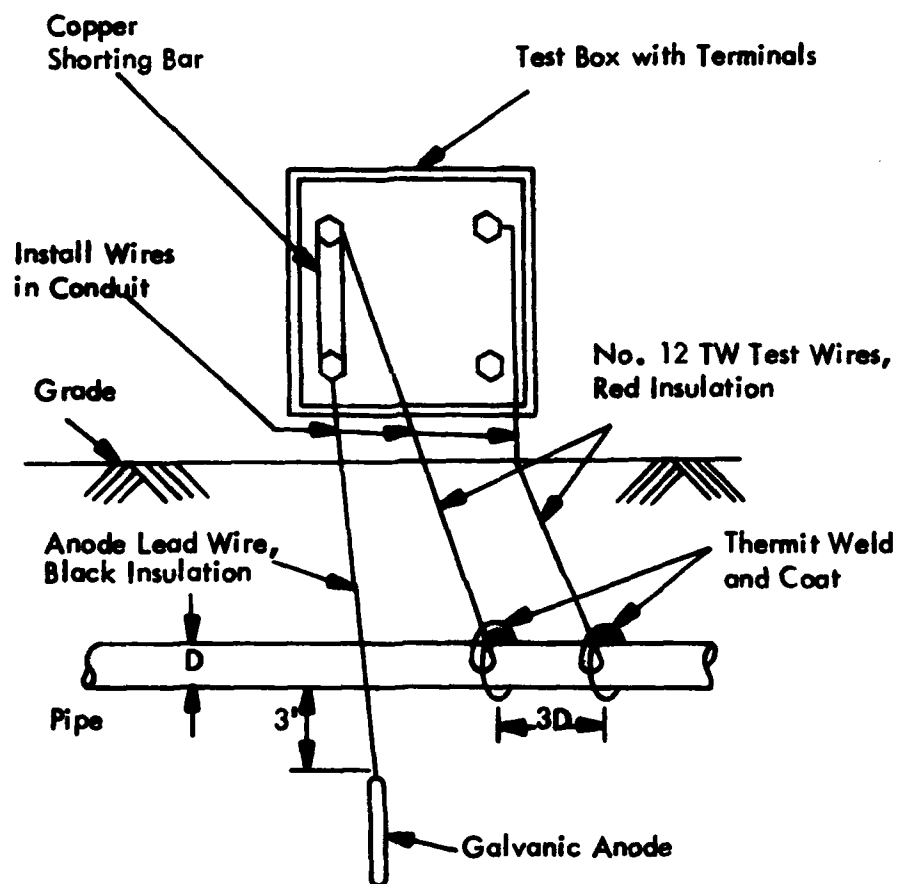


Figure 5-23
GALVANIC ANODE TEST STATION

A typical test station for a distributed bed of galvanic anodes on gathering wires is shown in Figure 5-24. Shunts may be used in place of copper shorting bars to facilitate current measurements.

5.8.1.8 Two-Wire Test Station. A typical two-wire test station (Figure 5-25) consists of two No. 12 TW test wires thermit-welded to the structure at a known separation, commonly three diameters on pipe. Free ends are terminated in a test box for use in measuring voltage drop and determining current flow.

5.8.1.9 Three-Wire Test Station. A three-wire test station (Figure 5-26) consists of a standard two-wire test station with an additional heavier test lead, often a No. 4 cable, thermit-welded to the structure. Heavier cable is included to facilitate future bonding, for example, where a future installation is to be installed.

5.8.1.10 IR Drop Calibration Test Station. Figure 5-27 shows a standard test station installation for IR Drop calibration, as can be applied to new pipeline construction and also older, existing lines. Through use of two posts on the latter, expensive trenching is eliminated. Care must be taken, however, that the distance "L" is not greater than the length of test leads which can be easily handled by the field man. The two posts can be located one each in the usual fences found on opposite sides of roads and highways. Standard color coding of wires eliminates guess work when measuring line current flow. While a typical two-wire test station would actually be sufficient to make necessary measurements, advantages offered by the four-wire installation, at a slight additional cost, are as follows:

1. The red and green leads can be used for accurate current measurements, after they have been calibrated by applying current to the black and white ones, to arrive at an ampere per millivolt factor for the test station. (In this way weight and composition of structure or an exact measurement of "L" are not required for the conversion of data to amperes.)
2. Simultaneous readings can be easily obtained at each test station, through use of two or three recording meters, indicating meters, or combinations. (For example, it might be desirable to get line current and pipe-to-soil reading at the same time, or either of these, or both; together with a voltage to a foreign structure.)
3. If it is necessary to connect the pipeline to another plant, one lead can be used, leaving the rest available for test purposes.
4. Continuity of each test lead can easily be checked out and, if one is broken, a drop is still available for current measurements.

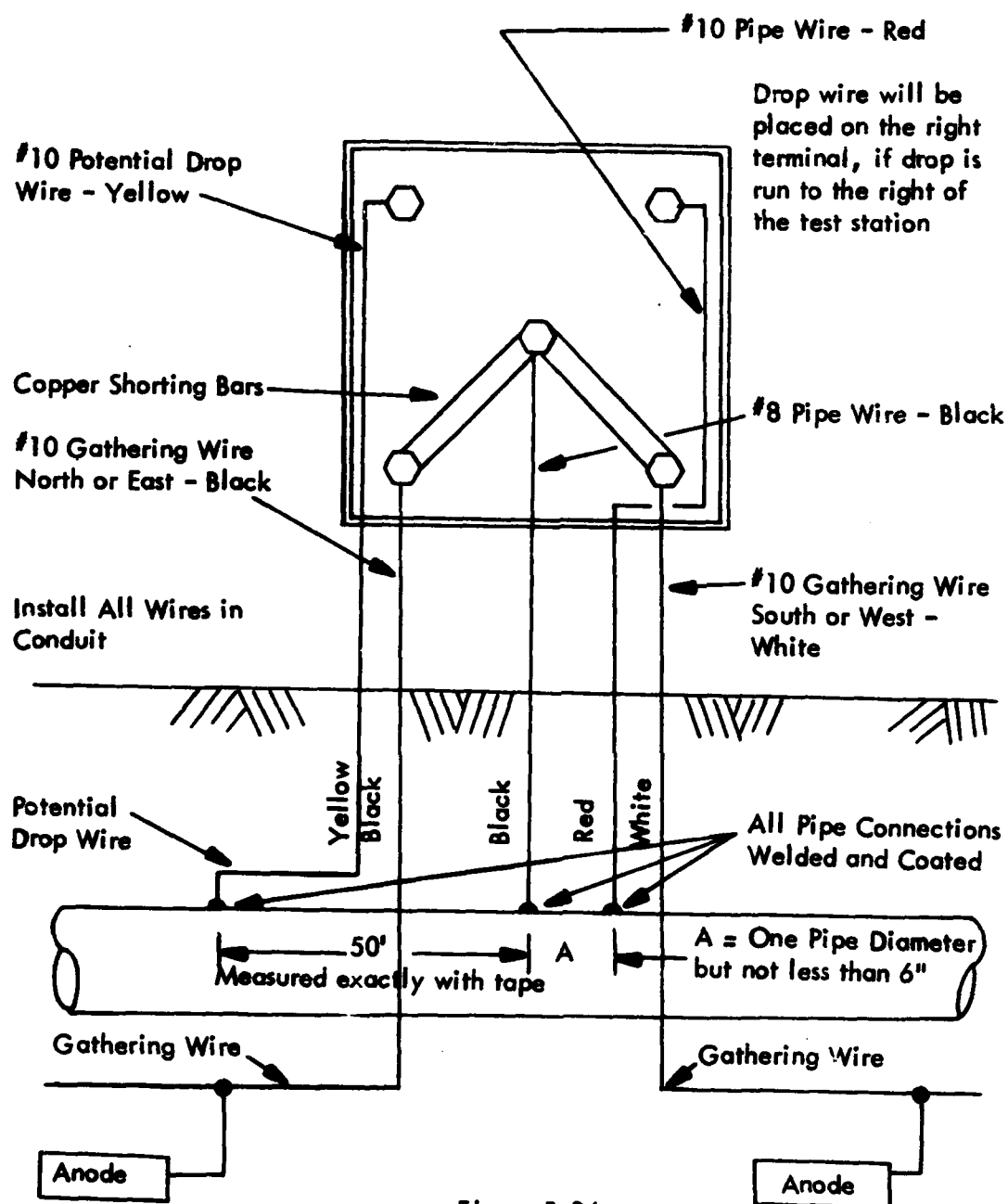


Figure 5-24
TEST STATION FOR GALVANIC ANODES ON GATHERING WIRE

Terminate Wires in Test Box

Two No. 12 TW Test Wires

Thermit Weld Wires As Shown,
Loop and Coat

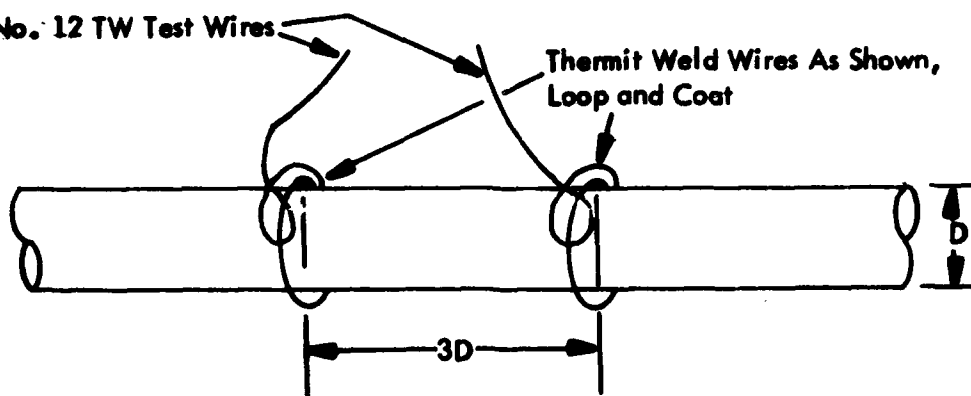
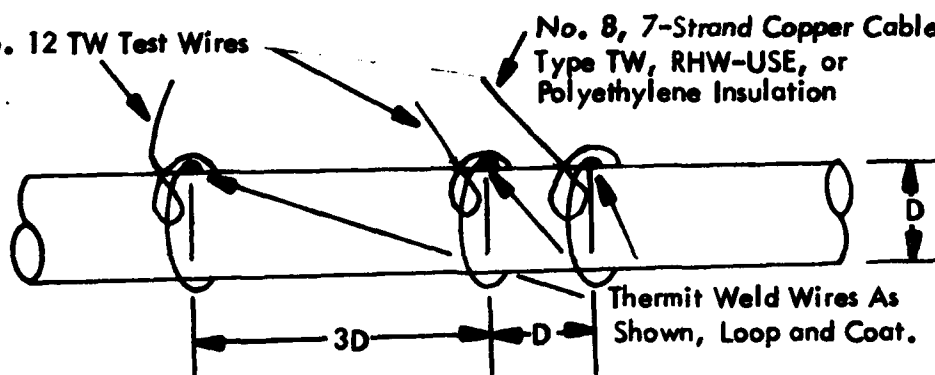


Figure 5-25

TWO-WIRE TEST STATION

Two No. 12 TW Test Wires

No. 8, 7-Strand Copper Cable,
Type TW, RHW-USE, or
Polyethylene Insulation



Terminate Wires in Test Box

Figure 5-26

THREE-WIRE TEST STATION

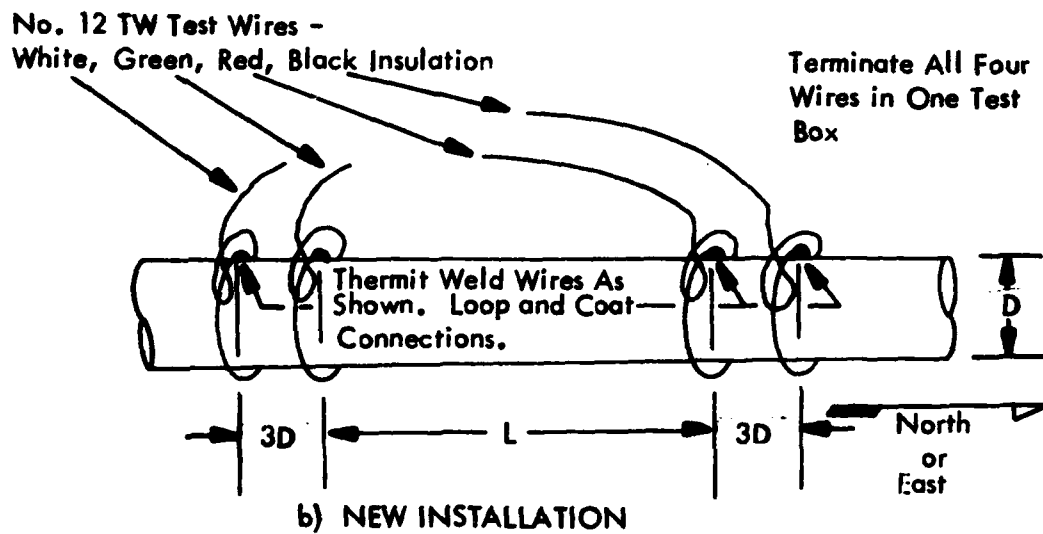
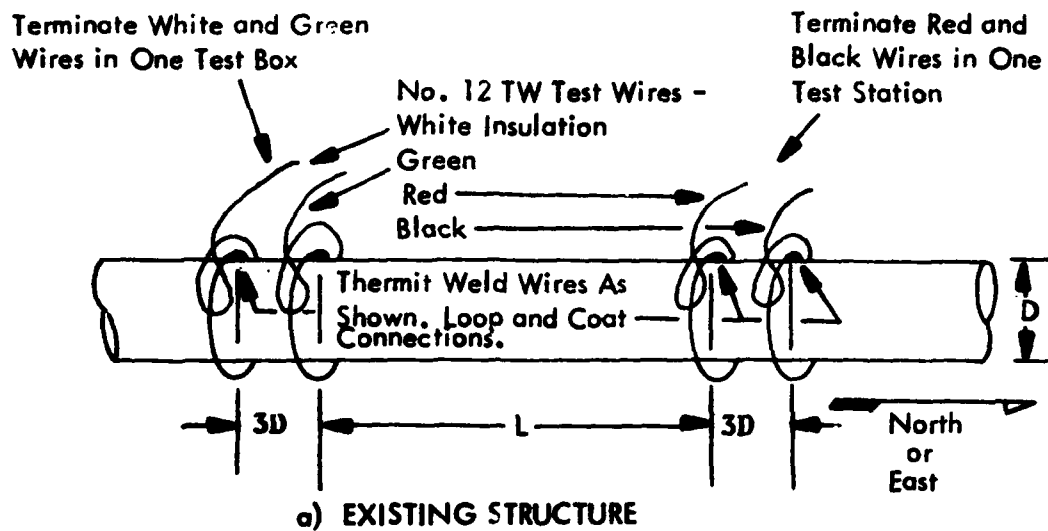


Figure 5-27
TEST STATIONS FOR MEASURING IR DROPS

The distance between the red and green wires designated as "L" can be equal in feet to some multiple of the resistivity per foot of pipe, a distance determined by physical characteristics of the pipeline right-of-way, or a convenient length chosen for purpose of standardization. (For example, a 100 feet distance could be used.)

5.9 CATHODIC PROTECTION. The National Association of Corrosion Engineers in their Standard RP-01-69, "Recommended Practice (for) Control of External Corrosion on Underground or Submerged Metallic Piping Systems" defines cathodic protection as:

"A technique to prevent the corrosion of a metal surface by making that surface the cathode of an electrochemical cell."

Cathodic protection does not really eliminate corrosion; it controls corrosion by keeping it entirely confined to selected pieces of metal which are replaced periodically. An artificial corrosion cell is formed by installing replaceable anodes which corrode causing current to flow from them through the electrolyte onto the protected metal, which thus becomes the cathode of this corrosion cell. (Cathodic protection current is superimposed on corrosion currents.) Current is either supplied to cathodic protection anodes by an external adjustable D.C. power source or natural voltage between anode material and protected structure material.

Cathodic protection is an effective, commonly used means of mitigating corrosion of buried and submerged metal structures.

Some criteria for determining when cathodic protection is needed and its limitations are mentioned here as an introduction.

5.9.1 Criteria for Using Cathodic Protection. As with other corrosion control methods, cathodic protection is applied to metal structures largely because it would be impractical to use more noble metals or non-metals and because the so-called "perfect" coating does not exist.

Cathodic protection may be required for economics, safety, or continuity of operation. Surveys to determine the need for cathodic protection are made on existing structures or estimated prior to construction of new facilities. Exact current requirements can never be determined until the structure has been built and in contact with its environment for from six months to two years. Factors considered in surveys follow no well-defined rules, but guidelines for sound engineering do exist. When cathodic protection is designed, it is generally most economical to use it in conjunction with

other means of control as coating, bonding, and insulation. This is especially true for new construction.

5.9.1.1 Department of Transportation Regulations. The Department of Transportation requires in its Minimum Federal Safety Standard (Title 49, Chapter 1, Section 192- see Appendix B.) that buried or submerged pipelines transporting natural or other gas must have a coating and cathodic protection system

"... designed to protect the pipeline in its entirety in accordance with this sub-part, installed and placed in operation within one year after completion of construction.

"(b) An operator need not comply with paragraph (a) of this section, if the operator can demonstrate by tests, investigation, or experience in the area of application, including, as a minimum, soil resistivity measurements and tests for corrosion accelerating bacteria, that a corrosive environment does not exist. However, within 6 months after an installation made pursuant to the preceding sentence, the operator shall conduct tests, including pipe-to-soil potential measurements with respect to either a continuous reference electrode or an electrode using close spacing, not to exceed 20 feet, and soil resistivity measurements at potential profile peak locations, to adequately evaluate the potential profile along the entire pipeline. If the tests made indicate that a corrosive condition exists, the pipeline must be cathodically protected in accordance with paragraph (a)(2) of this section.

"(c) An operator need not comply with paragraph (a) of this section, if the operator can demonstrate by tests, investigation, or experience that -

"(1) For a copper pipeline, a corrosive environment does not exist; or

"(2) For a temporary pipeline with an operating period of service not to exceed 5 years beyond installation, corrosion during the 5-year period of service of the pipeline will not be detrimental to public safety.

"(d) Notwithstanding the provisions of paragraph (b) or (c) of this section, if a pipeline is externally coated, it must be cathodically protected in accordance with paragraph (a) (2) of this section.

"(e) Aluminum may not be installed in a buried or submerged pipeline if that aluminum is exposed to an environment with a natural pH in excess of 8, unless tests or experience indicate its suitability in the particular environment involved."

Hence, if the operator cannot prove that cathodic protection is not required, he must install it. A similar requirement is covered in reference to transportation of hazardous

liquids by pipeline (Appendix B.). In addition to Federal regulations, all states either have or are preparing similar codes, some more stringent than the Federal ones. In these cases, the stricter state requirements must be followed.

5.9.1.2 National Association of Corrosion Engineers RP-01-69. In Standard RP-01-69, the National Association of Corrosion Engineers gives guidelines for determining the need for corrosion control of buried or submerged metallic structures.

"3.2 The decisions governing the need for corrosion control should be based on data obtained from corrosion surveys, operating records, prior test results with similar systems in similar environments, and on a study of design specifications, and engineering, operating, and economic requirements.

"3.2.1 Environmental and physical factors

"3.2.1.1 Corrosion rate of the particular metallic piping system in a specific environment...

"3.2.1.2 The nature of the product being transported and working pressure of the piping system as related to design specifications.

"3.2.1.3 Location of the piping system as related to density of population and frequency of visits by personnel.

"3.2.1.4 Location of the piping system as related to other facilities.

"3.2.1.5 Stray direct current sources foreign to the system...

"3.2.2 Economic Factors

"3.2.2.1 Costs of maintaining the piping system in service for its expected life...

"3.2.2.2 Contingent costs of corrosion...

"3.2.2.3 Costs of corrosion control..."

5.9.1.3 General. A typical method of determining if cathodic protection is required is summarized here.

First, a corrosion survey is performed at the site to determine if corrosion control (coating, insulation, cathodic protection, bonding, etc.) is economically warranted. Field tests, supplemented by laboratory analysis, are made of soils and waters in situ and of pertinent existing structures.

Stray current is investigated. The feasibility and cost of alternate types of cathodic protection, of substitute materials instead of cathodic protection, of coatings, or of no protection at all are weighed. On new construction, the survey should be initiated as soon as possible after site selection. This permits time for analysis of recommendations, necessary changes in design, and preparation of bidding documents.

Interpreting results of a corrosion survey is often complicated, as many factors must be considered. Generally, the value of survey results depends on the knowledge of the engineer, because experience is important in determining a potentially corrosive situation. Some guidelines to consider in interpreting a corrosion survey are given here. None of these guides are foolproof or always valid, because so many factors must be considered. Such things as galvanic cells, stray current, debris or cinders in the soil, differential environment cells, stresses on the metal structure, soil drainage - all these (existing and projected into the future) plus others (Section 3) affect a buried or submerged structure's corrosion rate.

a. Soil Resistivity. A general correlation exists between corrosivity and resistivity of soil (paragraph 3.2.3.2). This was summarized in Table 3-1, repeated here for convenience.

Table 3-1

<u>Resistivity Classification</u>	<u>Resistivity Range ohm-cm.</u>	<u>Anticipated Corrosion Activity</u>
Low	0 to 2,000	Severe
Medium	2,000 to 10,000	Moderate
High	10,000 to 30,000	Mild
Very High	Over 30,000	Unlikely

These values apply to individual soil resistivity measurements used as an indication or average of overall soil resistivity.

Another method of analysis requires numerous readings at selected locations in the area being considered. At each location, the lowest resistivity value is taken, the cumulative percent frequency is calculated, and results are plotted on extreme value probability paper (resistivity vs. frequency). From this graph, the probability of encountering soil of resistivity less than a predetermined value (such as 1000 ohm-centimeters) can be found. Soil corrosivity, based solely on resistivity, increases as the probability of encountering this value increases.

Pit depth analysis proceeds in a similar manner, with the structure excavated and pit depth measured at numerous locations. Values of the deepest pit at each location are taken, the cumulative percent frequency is calculated, and the results are plotted on extreme value probability paper (pit depth vs. frequency). The probable extent of corrosion of the entire structure can be predicted from this graph.

Soil resistivity probability and extent of corrosion are then correlated and used to estimate future corrosion problems. The results are used to determine which solution is better: corrosion control or eventual structure replacement.

It is emphasized that, while soil resistivity data determined from either method can often indicate a corrosive situation, many other factors must be considered.

b. Chemical Analysis. Chemical analysis is helpful in evaluating environmental corrosivity. Ferrous metals, for example, tend to depolarize in acid soils, and measurement of soil pH could, therefore, help to determine corrosivity. Sulfate content is another indicator. Sulfates are often found in soil where anaerobic bacteria are present and bacteriological corrosion could be anticipated. Generally, however, chemical analysis of soil is of limited value because of the wide variations in composition that can exist within a very small volume, changes that time can produce.

c. Voltage Measurements.

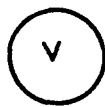
(1) General. Four basic voltage measurements, used to determine whether or not a metal is corroding (the need for cathodic protection), are shown in Figure 5-28. These are:

- a. Structure-to-electrolyte voltage
- b. Voltage drop along structure
- c. Structure-to-structure voltage
- d. Voltage drop through soil.

These and other field tests are described in paragraph 6.1.2.

Interpretation of these readings will indicate where, when and to what extent corrosion is occurring. Among other factors, location of the contact to electrolyte is crucial for accuracy. Soil resistance can affect voltage readings, although the greatest resistance is at the structure-to-electrolyte interface. The farther from the structure the half-cell is placed, the more IR drop through the electrolyte is included. Also, the farther the half-cell, the more structure surface explored in measurements.

Analysis of voltage readings can differentiate galvanic-electrochemical corrosion from stray current corrosion. Profiles of measurements taken at various points along a structure are often helpful in this respect. Structure-to-electrolyte voltages, plotted as a profile along the



Indicates Voltmeter
or Potentiometer

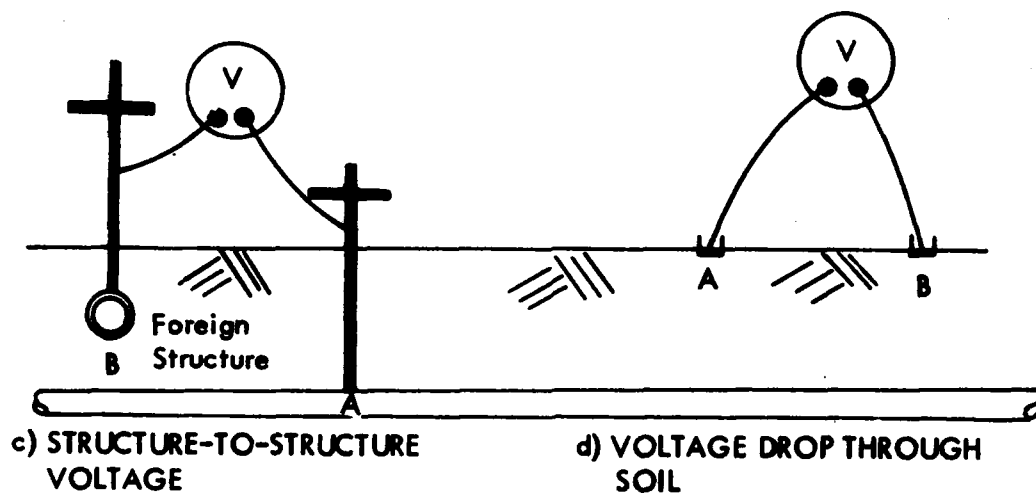
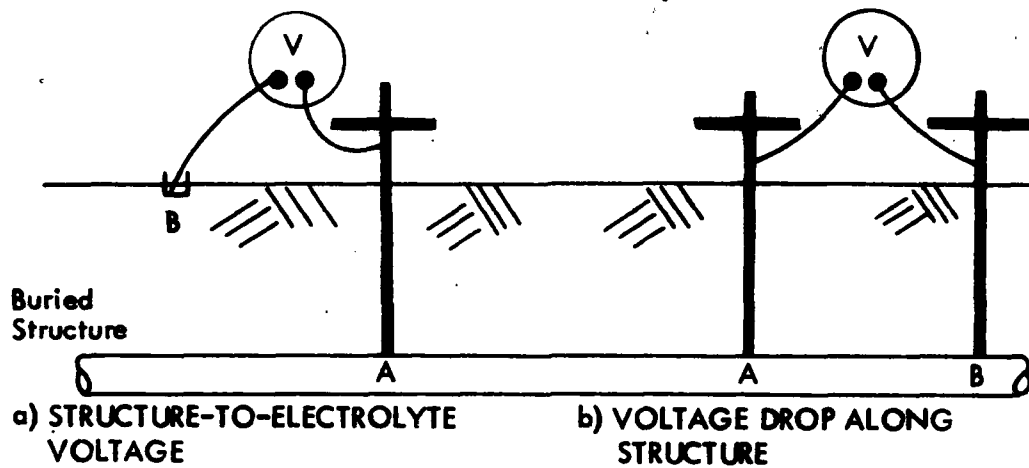


Figure 5-28
VARIOUS VOLTAGE MEASUREMENTS

structure, can indicate areas of current pickup and discharge. Current flow profiles are determined from voltage drops along the structure taken simultaneously at adjacent test points and plotted as X-Y coordinates. Profiles of simultaneous current and structure-to-electrolyte voltage at the same point help to determine areas of pickup and discharge. In combination, an effective analysis of structure can be obtained.

It is important to recognize that galvanic-electrochemical cells and stray currents can both be found together on a structure. An effective analysis will indicate which type(s) are producing corrosion.

(2) Galvanic and Electrochemical Corrosion. In galvanic and electrochemical cells, as metal becomes more positive (electrically) to its electrolyte, it becomes more cathodic. Structure-to-electrolyte potentials relative to a copper-copper sulfate (generally used) or other reference electrode in contact with electrolyte for an existing structure will, therefore, indicate corrosivity: They tell whether current is leaving or entering the structure. A single measurement is not conclusive since evaluation is based on a comparison of several readings.

Where no structure exists, structure-to-electrolyte potentials can be taken relative to a piece of metal partially buried in the ground. A piece of pipe or similar object might be used.

Table 5-12 gives anticipated corrosivity of ferrous metals for structure-to-soil potentials measured relative to a copper copper sulfate half-cell. It is important to recall that structure-to-soil potentials alone do not necessarily give a true indication of corrosivity.

Measurement of voltage along a structure can indicate if current is flowing there. From knowledge of the resistance of structure metal or an actual predetermined ampere per volt factor between two reference points, current flow can be computed. These measurements reveal average current flowing over the section tested. Small areas of pickup or discharge between test lead connections will not be detected.

Table 5-12

<u>Volts (Negative), Ferrous Metal Relative to a Copper- Copper Sulfate Half-Cell</u>	<u>Anticipated Corrosion Activity</u>
0.15 or below	Unlikely
0.15 to 0.45	Mild
0.45 to 0.55	Moderate
Over 0.55	Severe

The combination of structure-to-electrolyte voltages and voltage drops along the structure can help pinpoint galvanic or electrochemical cells. In addition, voltage can be measured between two electrically insulated sections of structure, or between two structures. This indicates whether current is flowing between two locations and direction of flow.

The fourth measurement, voltage drop through the electrolyte, can be used to estimate the tendency for current to flow through the earth. This is merely an indication and in itself is not conclusive.

(3) Stray Current Corrosion. Stray current corrosion is revealed by the same measurements as galvanic or electrochemical corrosion. Interpretation of structure-to-soil voltages, however, is different. Instead of measuring a natural potential difference as in a galvanic or electrochemical cell, structure-to-electrolyte voltage measures IR drop through the stray current circuit. As a result, stray current discharge depresses voltage, producing a less negative (and occasionally positive) result.

Fluctuating stray current measurement may require using special recorders which indicate values continuously. Analysis of this type corrosion includes time as a variable.

To get some idea as to whether or not stray current might be a problem prior to construction, "rosette" patterns

are made by measuring the potential between a stationary copper-copper sulfate half-cell and a movable copper-copper sulfate half-cell on a 50-foot radius circle. Measurements are taken at the eight major points of the compass. Resulting patterns and magnitude of readings indicate whether stray current, either fluctuating or steady, is likely to be present.

5.9.2 Limitations. Although cathodic protection is one of the most effective ways to control corrosion, the following limitations must be considered in design and operation:

1. Interference
2. Shielding
3. Amphoterics
4. Hydrogen embrittlement
5. Disbonding of coatings
6. Maintenance capabilities
7. Difficulties with auto-potential systems
8. Pre-engineered inadequacies
9. Economics

5.9.2.1 Interference. Neighboring structures sometimes experience excessive or objectionable interference from cathodic protection systems. This can be determined only by

application of test current (simulated cathodic protection) to structures to be protected. Bonds to foreign structures can mitigate many interference problems, but sometimes geometry, physical layout, or intercompany friction prevent this. If a buried or submerged pipe contains unbonded mechanical joints, for example, cathodic protection of a nearby structure could corrode the pipe; a bond between structures would not eliminate this. Structures in the area should be considered during design, and their owners contacted. When objectionable interference occurs, cathodic protection cannot be used.

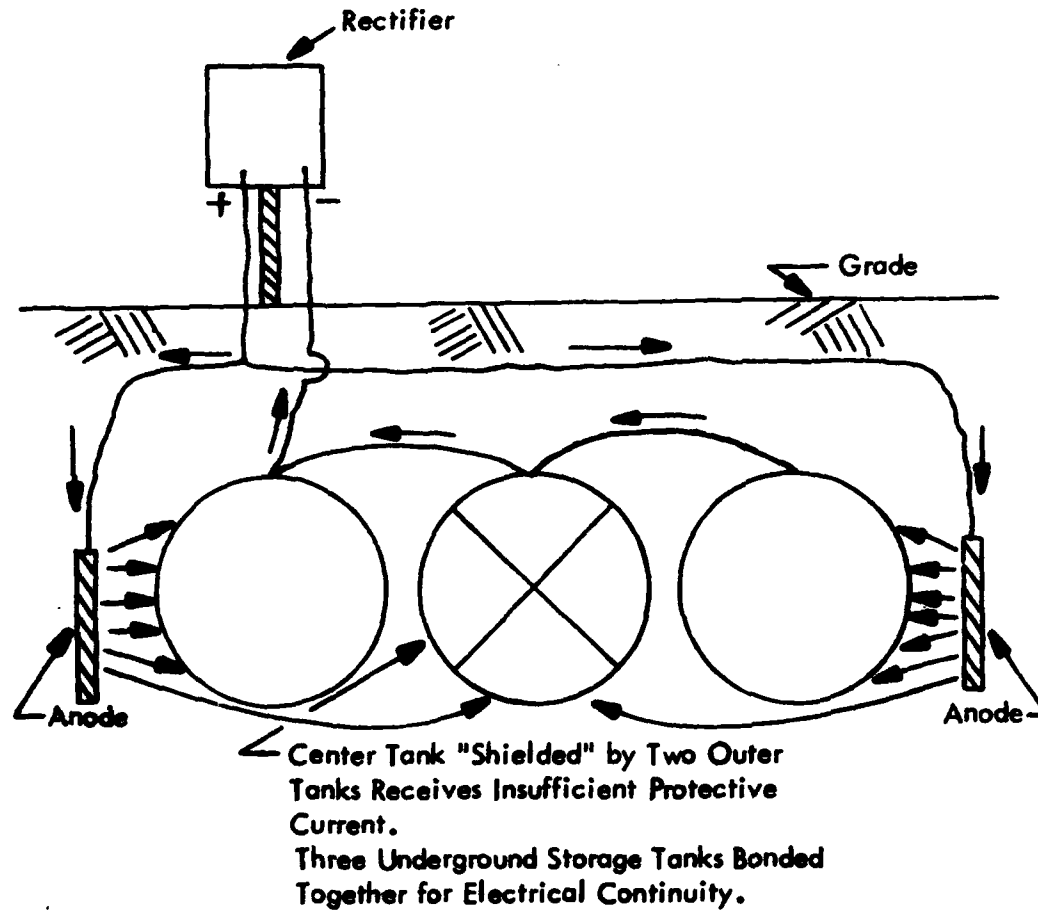
5.9.2.2 Shielding. A metal receiving cathodic protection must be in contact with an electrolyte (most commonly soil or water) for protective current to flow to its surface. This means that parts of a structure in air will not be protected. Internal structural surfaces will not be protected by cathodic protection current applied to outside surfaces (as with a pipeline inside a "shorted" casing). Also, when several structures to be protected are grouped closely together, relatively little current may flow to inner structures. This is called "shielding".

In Figure 5-29, for example, an impressed current system supplies three underground tanks with protective current. The center tank, shielded by the outer two, receives insufficient current for cathodic protection. Most of the current is intercepted by the two outer tanks. A different system, perhaps spacing anodes between tanks, is required for full protection.

5.9.2.3 Amphoterics. Because excessive cathodic protection voltages produce alkaline conditions at the protected metal surface, special care must be taken when protecting amphoteric metals. Aluminum and lead, each amphoteric, may suffer corrosion from alkaline material built up on their surfaces. For these metals, no voltage in excess of approximately 1.20 volts negative (relative to a copper-copper sulfate reference electrode) should be used. Correction of stray current conditions by bonding and cathodic protection systems must be carefully done where lead and aluminum are involved.

Corrosion of lead by cathodic reaction products can be controlled as long as protective current is held constant. If current is reduced or interrupted, alkaline material attacks lead. Since changes or interruptions in protective current are sometimes required, it is safest to keep all amphoteric metals in the voltage range below 1.20 volts.

NOTE: Arrows Indicate Flow of Protective Current



**Figure 5-29
ELECTRICAL SHIELDING**

5.9.2.4 Hydrogen Embrittlement. Some failures have been reported from hydrogen embrittlement of cathodically-protected structures. In order for this to occur, extremely high currents would be required for normally used steels. Table 5-13 gives accepted safe limits for ferrous-structure-to-electrolyte potentials in terms of electrolyte resistivities.

Table 5-13 (Reference 16)

Safe Limit of Structure-to-Electrolyte Potentials

<u>Electrolyte Resistivity</u> (ohm-cm.)	<u>Structure-to-Electrolyte Potential (E)</u> (volts, negative relative to Cu-CuSO ₄)
2000	1.8
3000	2.0
5000	2.2
10,000	2.6
15,000	2.8
20,000	3.0
30,000	3.35
40,000	3.6

Atomic hydrogen is frequently produced on metal surfaces cathodically protected. This is part of a normal cathode reaction, hydrogen evolution. Most hydrogen atoms combine, forming a polarization film of molecular hydrogen. Some atoms, however, are absorbed by the metal.

These atoms, at ambient temperatures, gather at lattice defects - voids or larger inclusions. There, pressure builds and in some cases eventual brittle failure occurs. Transgranular or intergranular cracking is possible.

Hydrogen embrittlement is common in steel, but only where high currents exist. Alloying can increase resistance to this type failure; it is generally not observed in low-alloy steels with tensile strengths below 60,000 psi.

5.9.2.5 Disbonding of Coatings. Another possible problem caused by hydrogen is disbonding of thin coatings. If excessive cathodic protection is applied to a structure, hydrogen may not merely form a polarization film. Hydrogen gas might bubble off creating great pressure at the edges of coating defects. Separation of coating from metal surface can result, producing increasing areas of bare metal as the coating disbonds.

Hydrogen gas will evolve only above the hydrogen over-voltage potential, a value which varies depending on metal and

environment conditions. For steel it is normally about 1.2 volts negative relative to a copper-copper sulfate electrode. With paints in water tanks and some other thin coatings, care should be taken to keep cathodic protection systems adjusted so that the structure potential is within a safe range. With the thicker coatings normally encountered underground, disbonding may occur only with poor quality coatings or under very severe soil (water) conditions.

5.9.2.6 Maintenance Conditions. A cathodic protection system maintenance program is necessary to hold electrical quantities to values specified by the original design.

At the same time, it can ensure the most economical use of current. Cathodic protection - like any other electrical system - cannot and will not operate continuously without maintenance.

An effective maintenance program costs money, although in general it is cheaper than possible system changes.

When the amount of current reaching metal surfaces under cathodic protection changes to a value too low to do the job, the polarization film may deteriorate. Then, a complex network of interconnected structures can become unbalanced, and corrosion failures may occur. And, the failure may occur in the structure which is intended to be protected, as well as in other bonded structures.

The density of current reaching metallic surfaces may be reduced by failure of the current source: rectifier or galvanic anodes.

Current may fail because: the anodes will eventually deteriorate; connections to anodes and/or between cables and wires sometimes fail; cables break at submerged or buried locations due to imperfections or damage to insulation; the rectifier unit may become inoperative or lose its source of supply.

Even when the D.C. current output from the source remains constant, other changes in the system may greatly reduce current density at metal surfaces under cathodic protection.

Among these changes: coatings may deteriorate or become damaged; foreign structures (not intended to be receiving cathodic protection) may come into electrical contact with the one under cathodic protection because of a physical contact due to careless construction or maintenance practices; an insulating joint might fail; or test leads may accidentally touch.

Conversely, a structure under cathodic protection may be overprotected even though the total D.C. protective current being supplied is still of its initial magnitude. This condition means that electric power is being used inefficiently, and is certainly most critical when large quantities of current are employed. Also, hydrogen embrittlement or coating disbonding could possibly result.

If new construction places foreign structures in the field of cathodic protection units, current exchange to these will cause additional drainage of protective current. Then, current intended for protection may actually protect the new structures. In extreme cases, more current may go to the foreign structure than to the one intended to be protected.

Therefore, to avoid adverse effects to protected or adjacent structures from system changes, an adequate maintenance program, set up by knowledgeable corrosion engineers, is essential. This must be considered a basic part of cathodic protection costs.

Also important is proper placement of system components (rectifiers, test stations, test access holes, and others) for ease of access. If structure orientation is such that cathodic protection system components are inaccessible, routine maintenance checks may be difficult or impossible. Cathodic protection may then become ineffective or even harmful. Improper locations may also interfere with base operations, if access requires temporary shutdown of a portion of the facilities.

5.9.2.7 Auto-Potential Systems. Auto-potential (automatic potential controlled) cathodic protection systems automatically vary rectifier current output to maintain a preset potential difference between the protected structure and a buried reference electrode.

Its effectiveness is limited by the sensing circuitry because potential is held constant only at the point where the reference electrode is placed. Since it is very likely that different conditions exist at other points on the structure, current supplied to maintain sufficient protection at the reference point may not adequately protect, or may overprotect, the remainder. Cinders and other debris in the soil, different types of soil, differential aeration, sulfate-reducing bacteria, coating holidays, and deterioration variations in the metal surface: these and other conditions can vary current requirements along a pipeline or other structure. As a result, the structure may experience coating disbonding from overprotection. It may fail from little or no protection.

Although suggested maintenance for these systems is low, auto-potential systems actually require annual inspections to avoid the problems discussed above. A high initial cost plus maintenance cost often makes auto-potential systems prohibitively expensive, compared to other means of corrosion control.

5.9.2.8 Pre-Engineered Cathodic Protection. Pre-engineered cathodic protection is used to minimize corrosion prevention costs. This is done because the value of facilities to be protected does not warrant much expenditure and/or for maximum competitive position. One application of these galvanic anode or impressed current systems is for buried, coated steel storage tanks. The effectiveness of pre-engineered cathodic protection generally depends on tank size and coating quality for a given number and configuration of anodes.

Pre-engineered protection is not effective in all installations. Being standardized, it is designed for adequate protection within certain environmental limits. Conditions outside these limits will generally prevent adequate protection. Further reduction in percent of installations receiving adequate protection can be expected from damage during installation, careless construction practices and changing conditions after installation. Post-installation evaluations are the only way to detect inadequately-protected structures.

Two standardization concepts are used. These are 1) a single design for all conditions and 2) selection from multiple designs for varying soil conditions. The multiple selection design is based on limited testing of soil samples. Some unusual conditions which require special treatment or on site investigation can also be detected. The single design will be less effective than the multiple selection (based on limited soil testing) design.

Some conditions which can reduce or render ineffective pre-engineered cathodic protection are:

1. Stray current
2. Very low soil resistivity

This will cause rapid anode dissipation and early loss of cathodic protection. Varying water tables can change resistivity after installation.

3. Varying soil resistivity

High-resistivity soil around anode with low-resistivity areas around parts of the tank may prevent sufficient current flow for adequate protection.

4. Very acid soil

5. Shielding

The structure can be shielded from protective current by configuration or foreign structures.

6. Excessive coating damage
 7. Ineffective dielectric insulation
Defective insulator or short-circuiting by contact with another metallic structure.
 8. Damaged or broken anode lead wires
 9. Damage to anode package
This may allow loss of special backfill for anode.
 10. High-resistance structure-to-anode connection
 11. Poor insulation on structure-to-anode connection
 12. Damage to any of the components during backfilling
- These conditions, singly or in combination, can prevent adequate cathodic protection.

Two types of predesigned system are available: impressed current or galvanic anodes. Pre-engineered impressed current systems usually rely on current rather than voltage control. A resistor is connected in series between the power source and each anode. This resistor is large enough to make the anode to ground resistance an insignificant percentage of total circuit resistance, and so is the controlling factor in current output. Typical is a 1,000 ohm resistor and a 110 volt power source to allow approximately 100 milliamperes from each anode.

Current controlled pre-engineered systems have a distinct advantage over voltage controlled (galvanic) systems. They function independently of soil resistivity. Soil resistivity is the major controlling factor in current output of galvanic anodes. Impressed current systems, however, are usually considerably more expensive than galvanic anodes and require more maintenance.

Half-wave rectification is commonly used in pre-engineered, self-regulating impressed current systems. This results in unbalanced A.C. on all grounds and interconnected utilities and can cause noise interference on buried communications cables. Impressed current systems are more likely to cause stray current problems than are galvanic anodes. Half-wave, current controlled rectifiers without isolating transformers are particularly bad in this respect.

Galvanic anode cathodic protection relies on a voltage (potential) difference between the anode and the structure to be protected. The controlling factor in cathodic protection current output is resistance of the anode to earth, which is, in turn, dependent on the soil resistivity. The resistance to earth of the protected structure is usually not significant, particularly for larger structures, when compared to the resistance of the rest of the circuit. If environment or mechanical conditions require high-current output for adequate cathodic protection, limited driving potential of galvanic anodes may not be sufficient to provide the needed current.

Pre-engineered systems, then, have limited applicability. If the structures to be protected are relatively small or inexpensive (i.e. short lengths of buried pipe or small buried tanks), current requirement tests may not be economically feasible. Soil tests should be conducted to evaluate the need for cathodic protection. If it is decided to use pre-engineered cathodic protection, initial savings must be balanced against expected replacement costs and safety hazard caused by partially-effective cathodic protection.

5.9.2.9 Economics. Where safety, success of the mission, and shutdown time required for structure replacement or repairs are not of concern, simple economics may dictate whether or not cathodic protection should be used. In general, the least expensive, easiest to maintain and most practical system is to apply a good quality coating to a new structure and then to use cathodic protection to eliminate corrosion at the inevitable breaks in the coating. This method requires much less current than cathodic protection alone. An economic comparison of several methods of corrosion control is found in paragraph 2.5; this applies to economics and cathodic protection. Figure 2-3 compares costs of several types of cathodic protection.

5.10 ANODIC PROTECTION. Anodic protection is a very limited and relatively new means of corrosion control. It has found application only within the last ten years or so. It is mainly used to protect steel or stainless steel in sulfuric acid. Anodic protection can be applied only to metals exhibiting active-passive behavior. The protected metal is kept passive (paragraph 3.8) by application of an anodic current. The level of current required is maintained by a potentiostat. A typical example of anodic protection of a storage tank is shown in Figure 5-30. The structure is anodic to the auxiliary electrode (usually platinum or platinized metal). A reference electrode, such as standard silver-silver chloride, and potentiostat control the anodic current level. Control of corrosion - not elimination - is achieved because the rate of corrosion for a passive metal is far lower than for the active metal.

5.10.1 Advantages. Advantages of anodic protection as a means of corrosion control are:

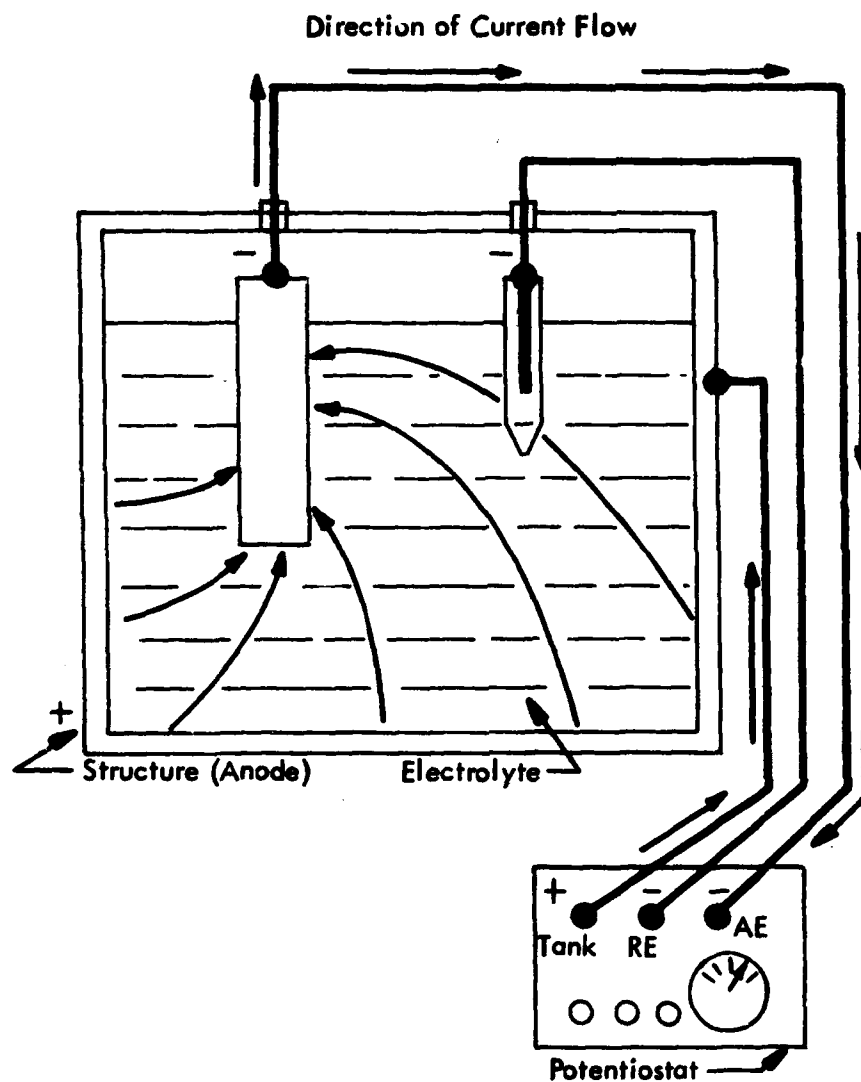
Generally easy to predict effectiveness and to design;

Good throwing power; can protect complex structures with few electrodes, if properly placed;

Low operating costs, with little current required even in severe corrosives;

Effective in strong corrosives, such as sulfuric acid;

Easily monitored; adequate protection determined from amount of protective current;



AE = Auxiliary Electrode (Cathode)
 RE = Reference Electrode

Figure 5-30
 ANODIC PROTECTION

Often possible to apply current intermittently. This facilitates protecting several structures with the same power source.

5.10.2 Limitations. Application of anodic protection is limited for several reasons:

- Malfunctions can cause increased corrosion of metal to be protected;
- High installation and initial operating costs;
- Applicable only to active-passive metals such as iron, steel, and aluminum in passivating electrolytes;
- Requires power source;
- Limited in-service experience records;
- More complicated circuitry and expensive equipment required.

5.11 ELECTRICAL GROUNDING.

5.11.1 What Grounding is. Electrical grounding is designed to provide a low-resistance path to ground for fault currents. This limits potentials to values safe to personnel. Grounding electrodes must be corrosion-resistant and good electrical conductors. Above all, they must provide sufficient area in contact with soil so that the current resistance path will be within allowable limits for the particular application. Grounding methods described herein do not apply to hydroelectric generating plants, substations, switching stations, and other similar installations.

5.11.2 Grounding and Corrosion. Most grounding systems are constructed of copper. Copper is a good conductor, corrosion-resistant in many soils, and relatively inexpensive. Very little corrosion difficulty was experienced as a result of this practice in the early years of electric power distribution, because most electrical circuits were installed overhead, utilizing wooden structures.

As areas became more thickly populated, electrical distribution systems were installed underground. The effects of copper grounding systems on other metal utilities were not considered. As a result, severe galvanic corrosion has been experienced. Since most construction metals are anodic to copper, they will corrode to protect copper when coupled together in a suitable environment. (This is why copper appears to be so resistant to corrosion in so many environments.)

The most commonly used metals of construction for underground use are iron, aluminum, lead, and zinc. The average potential difference between these metals and copper when coupled in suitable electrolyte as soils or water is given in Table 5-14.

Table 5-14

Galvanic Couple Potentials

<u>Galvanic Couple</u>	<u>Potential Difference (Volts)</u>
Iron-copper	0.55
Aluminum-copper	1.55
Lead-copper	0.45
Zinc (galvanizing)-copper	0.90

Table 5-14 indicates relative driving force to corrode for the given metal couples; other conditions being equal, corrosion rate is proportional to potential difference.

5.11.3 Grounding Systems.

5.11.3.1 Neutral Conductor Networks. The neutral conductor for underground electrical distribution systems is often bare copper cables. Neutrals of transformers and metal housings for electrical apparatus are often grounded to the neutral conductor. For water-cooled transformers, water piping is tied to the neutral cable through the transformer. Lead-sheathed cables are also grounded to the neutral conductor cable. Residential hot water tanks, and other appliances, form connections between neutral cables and water piping.

The galvanic couple formed by these connections under suitable environmental conditions can rapidly corrode lead-sheathed cable and water piping. Lead cable will generally experience corrosion first, although the voltage difference between the lead and copper is slightly lower than between steel and copper. This is true because lead has an extremely high deterioration rate (about 75 pounds per ampere-year).

Such couplings can be greatly reduced during design, by specifying that buried neutral conductor and cables connections between ground rods be covered with an insulating jacket such as vinyl or other suitable material. This reduces conductance to earth and can be compensated for by additional ground rods.

5.11.3.2 Service Piping for Utilities. Using cold water piping to ground electrical-service entrance equipment is common practice. Cold water piping is also used for grounding electrical equipment in many industrial applications. Generally, alternating current which may flow as a result of using the piping system for grounding will not damage the piping to any extent. Direct current, however, can cause severe corrosion to piping, and tie-ins producing it should be avoided.

In addition, when the secondary neutral of a transformer serving more than one establishment is grounded to cold water piping, galvanic corrosion can occur. For example, one building used to ground the neutral conductor has copper water service. Another, grounding the same conductor, has galvanized water service. The copper service is connected to the adjacent galvanized service even if both services are insulated from the water main. In this case, the galvanized service pipe will corrode to protect the copper pipe. In order to avoid this, individual transformers could be installed for each building. However, such a practice would be too costly and is not feasible. This problem can best be solved by avoiding the use of dissimilar metals during construction. For existing systems, insulating joints should be installed or the service lines replaced with like metal as they fail, to avoid corrosion from dissimilar conditions.

5.11.3.3 Buried Metal Grounding Plates. Copper grounding plates produce much the same corrosion problems as copper rods, intensified by the larger surface area of plates. This means larger cathode-to-anode area ratio and increased corrosion from the "area effect".

Using zinc or galvanized steel grounding plates will prevent this because zinc is anodic to ferrous metals. The zinc will corrode, but grounding electrodes can easily be designed for a life of 25 to 50 years.

Another alternate is stainless steel or stainless-clad ground rods, which are relatively close in potential to most underground structures.

Aluminum is not recommended for grounding. If used as an electrical conductor, it should be completely insulated from soil and water, or other moisture.

5.11.4 Grounding Materials - Pro and Con. Copper is the most widely used material for grounding systems, not necessarily because it is the best. It formerly was the only metal used for grounding and is still specified in most electrical codes. These codes are difficult to change, even though alternate materials may be better. Copper, as noted earlier, is cathodic to most structural metals and can cause serious corrosion when used in grounding systems. Bare copper conductors are frequently used to connect ground rods (even non-copper rods) and increase area in contact with soil. This practice, which increases corrosion of other structural materials, should be avoided especially when copper is not the ground rod material. Insulated cable will help avoid serious corrosion from galvanic couples.

If codes require copper grounds, electrolytic cells, gaps, or other provisions for high current flow should be made to

minimize galvanic corrosion.

Zinc or galvanized ground rods, when connected to bare structural metals, create galvanic cells. However, zinc, unlike copper, becomes the anode of such a couple and corrodes to protect most structural metals.

Consideration must be given to the life of zinc ground rods as zinc is greatly affected by local environmental conditions. Zinc rods properly installed in an approved backfill material (such as 50 percent bentonite and 50 percent hydrated gypsum) can be expected to have an operating efficiency of 90 percent. This means, that during its useful life, 90 percent of the zinc consumed will be apparent as useful output current, while the remaining 10 percent will be used in self-corrosion processes. A zinc anode can continue to be used for grounding purposes until the zinc surrounding the steel core is at least 85 percent consumed. If longer life is desired, it may be obtained by using two or more ground rods in the same augered hole. The expected life will then be approximately that of one anode multiplied by the number of anodes in the same hole. Another solution would be to use a larger ground rod.

Galvanized steel ground rods react similarly to zinc rods, but the thin zinc coating is rapidly consumed.

Stainless steel ground rods are also used. These do not provide ferrous structural materials with the same galvanic corrosion protection as zinc. However, they do not corrode other structures as copper grounds. Steel, of course, is subject to soil corrosion, but can provide satisfactory life for many applications.

Ground rods made of other metals, such as aluminum, have been given some attention. Copper, zinc, and steel, however, remain the materials most generally accepted.

5.11.5 Isolation of Buried Structures From Grounds.

Copper grounding systems have an adverse effect on cathodic protection systems. The degree of effectiveness varies with the area of copper in contact with the soil. Extremely high values of current will be required to protect underground structures connected to copper grounds. The reason is that protective current flows to copper where it is least required. This is usually true where different metals are coupled together and cathodically protected. If the underground structures were electrically isolated from the copper grounding system, or if zinc or stainless steel ground rods were employed, the required protective current would be much less.

5.12 ENVIRONMENT. Altering the environment can sometimes reduce corrosion, but the "perfect" environment, like the

"perfect" coating, has not been discovered. Removing impurities or dissolved materials, altering chemical compositions, or substituting an entirely different electrolyte can sometimes reduce corrosion problems. However, environmental composition is extremely difficult and expensive to control outside the laboratory, and small impurities can produce disastrous results. For example, on-grade storage tanks are sometimes placed on a layer of sand to prevent soil corrosion. Small clods of earth can easily get mixed in the sand during construction, and earth in contact with the metal is anodic to the rest of the structure. Unless additional protection such as cathodic protection is employed, corrosion concentrates at this point because of the "area effect".

In general, altering the environment is effective only when used with other methods of corrosion control.

5.12.1 Advantages of Uniform Environment. When pipes are installed in trenches, the backfill is usually a mixture of various soil types due to the nature of trenching operations. This mixture can cause differential environment corrosion and should be avoided. A selected backfill, uniform in composition and containing no cinders or other debris, can often help minimize differential environment corrosion. It does not guarantee homogeneity, however, because moisture and oxygen content as well as other impurities are not practically controlled.

Similar problems are encountered in water or other liquids. Dissolved material often concentrates in one area of a structure (such as corners in tanks, crevices, or the bottom of pipes) producing concentration cell corrosion. Elimination of dissolved material or agitation to provide uniform distribution can often mitigate this.

5.12.1.1 Use of Sand as a Backfill. Sand used as a backfill should be free from clay, rocks, organic matter, and mineral salts. Individual particles usually vary from 0.002 to 0.004 inch in size. Many sands contain impurities and should be washed. Sand of high resistivity, 25,000 ohm-centimeters or higher, is desirable. Use of local sand of lower resistivity may sometimes be more economical than importation of higher resistivity sand. When low resistivity sand is used, a good coating supplemented by cathodic protection may be necessary because of inevitable impurities present.

5.12.1.2 Effects of Cinders and Debris. Cinders and foreign matter can damage buried or submerged structures contacting them. Sharp fragments can penetrate coatings, producing holidays where corrosion concentrates. Foreign matter deposited on metal surfaces can cause concentration cell (paragraph 4.3.2) or crevice corrosion (paragraph 4.3.3).

Metallic debris contacting structures can produce galvanic corrosion. Cinders are especially harmful in this respect, because they contain some unburned carbon, cathodic to ferrous metals. The large potential difference between carbon and iron or steel, approximately 2.0 volts, can produce rapid corrosion. In addition, the shielding effect of cinders or other metal in contact prevents cathodic protection current from reaching the structure surface below.

5.12.2 Drainage. Standing water from rain or other sources can produce serious corrosion. Crevices and other areas where water pockets can form should be eliminated in the design phase. If this is not feasible, proper drainage must be provided.

5.12.3 Ducts and Tunnels. Ducts or tunnels are sometimes used to house lead-sheath cable and other utilities. These provide isolation from soil or water and prevent corrosion by eliminating the electrolyte. Care must be taken to avoid seepage of water into these structures, because serious corrosion can result. Cathodic protection is frequently employed to protect lead-sheath cable installed in ducts (paragraph 4.15.12).

Tunnels are very expensive, but there are times when a tunnel may be the best answer. This is particularly true when many utilities and perhaps a pedestrian passage share the same tunnel.

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APPENDIX A.

GLOSSARY OF CORROSION TERMS

(*Definitions from NACE Standard RP-01-69)

Adsorption. The taking up of one substance at the surface of another. The tendency of all solids to condense upon their surfaces a layer of any gas or solute which contact such solids.

Aeration cell (oxygen cell). An electrolytic cell in which a difference in oxygen concentration at the electrodes exists, producing corrosion.

Amphoterics. Materials subject to attack by both acid and alkaline environments. Aluminum, zinc, and lead, commonly used in construction, are examples.

Anaerobic. Free of air or uncombined oxygen; an aerobic bacteria are those which do not use oxygen in their life cycle.

Anion. A negatively charged ion which migrates toward the anode under influence of a potential gradient.

*Anode. An electrode at which oxidation of its surface or some component of the solution is occurring. Antonym:cathode.

*Bell hole. An excavation to expose a buried structure.

Cathode. An electrode at which reduction of its surface or some component of the solution is occurring. Antonym:anode.

Cathodic corrosion. Corrosion resulting from a cathodic condition of a structure, usually caused by the reaction of alkaline products of electrolysis with an amphoteric metal.

*Cathodic Protection. A technique to prevent the corrosion of a metal surface by making that surface the cathode of an electrochemical cell.

Cation. A positively charged ion of an electrolyte which migrates toward the cathode under the influence of a potential gradient.

Concentration cell. An electrolytic cell in which a difference in electrolyte concentration exists between anode and cathode, producing corrosion.

*Continuity bond. A metallic connection that provides electrical continuity.

*Corrosion. The deterioration of a material, usually a metal, because of a reaction with its environment.

*Current density. The current per unit area.

*Electrical isolation. The condition of being electrically separated from other metallic structures or the environment.

*Electro-osmotic effect. Passage of a charged particle through a membrane under the influence of a voltage. Soil may act as the membrane.

*Electrode potential. The potential of an electrode as measured against a reference electrode. The electrode potential does not include any loss of potential in the solution due to current passing to or from the electrodes, i.e. it represents the reversible work required to move a unit charge from the electrode surface through the solution to the reference electrode.

Electrolyte. A chemical substance or mixture, usually liquid, containing ions that migrate in an electric field. Examples are soil and seawater.

Electromotive force series (EMF series). A list of elements arranged according to their standard electrode potentials, the sign being positive for elements having potentials that are cathodic to hydrogen and negative for those elements having potentials that are anodic to hydrogen.

*Foreign structure. Any structure that is not intended as a part of the system of interest.

*Galvanic anode. A metal which, because of its relative position in the galvanic series, provides sacrificial protection to metal or metals that are more noble in the series, when coupled in an electrolyte. These anodes are the current source in one type of cathodic protection.

Galvanic cell. A corrosion cell in which anode and cathode are dissimilar conductors, producing corrosion because of their innate difference in potential.

*Galvanic series. A list of metals and alloys arranged according to their relative potentials in a given environment.

*Holiday. A discontinuity of coating that exposes the metal surface to the environment.

Hydrogen overvoltage. Voltage characteristic for each metal-environment combination above which hydrogen gas is liberated.

*Impressed current. Direct current supplied by a power source external to the electrode system.

*Insulating coating system. All components comprising the protective coating, the sum of which provides effective electrical insulation of the coated structure.

*Interference bond. A metallic connection designed to control electrical current interchange between metallic systems.

Ion. Electrically charged atom or molecule.

*IR drop. The voltage across a resistance in accordance with Ohm's Law.

*Line current. The direct current flowing on a pipeline.

Local action. Corrosion caused by local cells on a metal surface.

Mill scale. The heavy oxide layer formed during hot fabrication or heat-treatment of metals. The term is applied chiefly to iron and steel.

Molality. Concentration of a solution expressed as the number of gram molecules of the dissolved substance per 1000 grams of solvent.

pH. A measure of hydrogen ion activity defined by $\text{pH} = \log_{10} (1/a\text{H}^+)$ where $a\text{H}^+$ = hydrogen ion activity = molal concentration of hydrogen ions multiplied by the mean ion activity coefficient (= 1 for simplified calculations).

Polarisation. The deviation from the open circuit potential of an electrode resulting from the passage of current.

*Reference electrode. A device whose open circuit potential is constant under similar conditions of measurement.

*Reverse-current switch. A device that prevents the reversal of direct current through a metallic conductor.

*Stray current. Current flowing through paths other than the intended circuit.

*Stray current corrosion. Corrosion resulting from direct current flow through paths other than the intended circuit.

*Structure-to-electrolyte voltage. (also structure-to-soil potential or pipe-to-soil potential). The voltage difference between a buried metallic structure and the electrolyte which is measured with a reference electrode in contact with the electrolyte.

*Structure-to-structure voltage. (also structure-to-structure potential). The difference in voltage between metallic structures in a common electrolyte.

*Voltage. An electromotive force, or a difference in electrode potentials expressed in volts.

APPENDIX B.

DEPARTMENT OF TRANSPORTATION REGULATIONS

Title 49 - Transportation

**Chapter 1-Hazardous Materials Regulations Board, Department of Transportation.
(Docket No. OPS-5; Amdt. 192-4)**

Part 192-Transportation of Natural and other gas by pipeline: Minimum Federal safety standards

Subpart 1-Requirements for Corrosion Control

192.451 Scope.

This subpart prescribes minimum requirements for the protection of metallic pipelines from external, internal, and atmospheric corrosion.

192.453 General.

Each operator shall establish procedures to implement the requirements of this subpart. These procedures, including those for the design, installation, operation and maintenance of cathodic protection systems, must be carried out by, or under the direction of, a person qualified by experience and training in pipeline corrosion control methods.

192.455 External corrosion control: buried or submerged pipelines installed after July 31, 1971.

(a) Except as provided in paragraphs (b) and (c) of this section, each buried or submerged pipeline installed after July 31, 1971 must be protected against external corrosion, including the following:

(1) It must have an external protective coating meeting the requirements of 192.46.

(2) It must have a cathodic protection system designed to protect the pipeline in its entirety in accordance with this subpart, installed and placed in operation within one year after completion of construction.

(b) An operator need not comply with paragraph (a) of this section, if the operator can demonstrate by tests, investigation, or experience in the area of application, in-

cluding, as a minimum, soil resistivity measurements and tests for corrosion accelerating bacteria, that a corrosive environment does not exist. However, within 6 months after an installation made pursuant to the preceding sentence, the operator shall conduct tests, including pipe-to-soil potential measurements with respect to either a continuous reference electrode or an electrode using close spacing, not to exceed 20 feet, and soil resistivity measurements at potential profile peak locations, to adequately evaluate the potential profile along the entire pipeline. If the tests made indicate that a corrosive condition exists, the pipeline must be cathodically protected in accordance with paragraph (a) (2) of this section.

(c) An operator need not comply with paragraph (a) of this section, if the operator can demonstrate by tests, investigation, or experience that-

(1) For a copper pipeline, a corrosive environment does not exist; or

(2) For a temporary pipeline with an operating period of service not to exceed 5 years beyond installation, corrosion during the 5-year period of service of the pipeline will not be detrimental to public safety.

(d) Notwithstanding the provisions of paragraph (b) or (c) of this section, if a pipeline is externally coated, it must be cathodically protected in accordance with paragraph (a) (2) of this section.

(e) Aluminum may not be installed in a buried or submerged pipeline if that aluminum is exposed to an environment with a natural pH in excess of 8, unless tests or experience indicate its suitability in the particular environment involved.

192.457 External corrosion control: buried or submerged pipelines installed before August 1, 1971.

(a) Except for buried piping at compressor, regulator, and measuring stations, each buried or submerged transmission line installed before August 1, 1971, that has an effective external coating must, not later than August 1, 1974, be cathodically protected along the entire area that is effectively coated, in accordance with this subpart. For the purposes of this subpart, a pipeline does not have an effective external coating if its cathodic protection current requirements are substantially the same as if it were bare. The operator shall make tests to determine the cathodic protection current requirements.

(b) Except for cast iron or ductile iron, each of the following buried or submerged pipelines installed before August 1, 1971, must, not later than August 1, 1976, be cathodically protected in accordance with this subpart in areas in which active corrosion is found:

- (1) Bare or ineffectively coated transmission lines.
- (2) Bare or coated pipes at compressor, regulator, and measuring stations.
- (3) Bare or coated distribution lines. The operator shall determine the areas of active corrosion by electrical survey, or where electrical survey is impractical, by the study of corrosion and leak history records, by leak detection survey, or by other means.
- (c) For the purpose of this subpart, active corrosion means continuing corrosion which, unless controlled, could result in a condition that is detrimental to public safety.

192.459 External corrosion control: examination of buried pipeline when exposed.

Whenever an operator has knowledge that any portion of a buried pipeline is exposed, the exposed portion must be examined for evidence of external corrosion if the pipe is bare; or if the coating is deteriorated. If external corrosion is found, remedial action must be taken to the extent required by 192.483 and the applicable paragraphs of 192.485, 192.487, or 192.489.

192.461 External corrosion control: protective coating.

(a) Each external protective coating, whether conductive or insulating, applied for the purpose of external corrosion control must-

- (1) Be applied on a properly prepared surface;
- (2) Have sufficient adhesion to the metal surface to effectively resist under-film migration of moisture;
- (3) Be sufficiently ductile to resist cracking;
- (4) Have sufficient strength to resist damage due to handling and soil stress; and
- (5) Have properties compatible with any supplemental cathodic protection.

(b) Each external protective coating which is an electrically insulating type must also have low moisture absorption and high electrical resistance.

(c) Each external protective coating must be inspected just prior to lowering the pipe into the ditch and backfilling, and any damage detrimental to effective corrosion control must be repaired.

(d) Each external protective coating must be protected from damage resulting from adverse ditch conditions or damage from supporting blocks.

(e) If coated pipe is installed by boring, driving, or other similar method, precautions must be taken to minimize damage to the coating during installation.

192.463 External corrosion control: cathodic protection.

(a) Each cathodic protection system required by this subpart must provide a level of cathodic protection that complies with one or more of the applicable criteria contained in Appendix D of this subpart. If none of these criteria is applicable, the cathodic protection system must provide a level of cathodic protection at least equal to that provided by compliance with one or more of these criteria.

(b) If amphoteric metals are included in a buried or submerged pipeline containing a metal of different anodic potential-

(1) The amphoteric metals must be electrically isolated from the remainder of the pipeline and cathodically protected; or

(2) The entire buried or submerged pipeline must be cathodically protected at a cathodic potential that meets the requirements of Appendix D of this part for amphoteric metals.

(c) The amount of cathodic protection must be controlled so as not to damage the protective coating or the pipe.

192.465 External corrosion control: monitoring.

(a) Except where impractical on off-shore pipelines, each pipeline that is under cathodic protection must be tested at least once each calendar year, but with intervals not exceeding 15 months, to determine whether the cathodic protection meets the requirements of 192.463. However, if tests at those intervals are impractical for separately protected service lines or short sections of protected mains, not in excess of 100 feet, these service lines and mains may be surveyed on a sampling basis. At least 10 percent of these protected structures, distributed over the entire system must be surveyed each calendar year, with a different 10 percent checked each subsequent year, so that the entire system is tested in each 10-year period.

(b) At intervals not exceeding 2 months, each cathodic protection rectifier or other impressed current power source must be inspected to ensure that it is operating.

(c) At intervals not exceeding 2 months, each reverse current switch, each diode, and each interference bond whose failure would jeopardize structure protection, must be electrically checked for proper performance. Each other interference bond must be checked at least once each calendar year, but with intervals not exceeding 15 months.

(d) Each operator shall take prompt remedial action to correct any deficiencies indicated by the monitoring.

(e) After the initial evaluation required by paragraphs (b) and (c) of 192.455 and paragraph (b) of 192.457, each operator shall, at intervals not exceeding 3 years, reevaluate its unprotected pipelines and cathodically protect them

in accordance with this subpart in areas in which active corrosion is found. The operator shall determine the areas of active corrosion by electrical survey, or where electrical survey is impractical, by the study of corrosion and leak history records, by leak detection survey, or by other means.

192.467 External corrosion control: electrical isolation.

(a) Each buried or submerged pipeline must be electrically isolated from other underground metallic structures, unless the pipeline and the other structures are electrically interconnected and cathodically protected as a single unit.

(b) An insulating device must be installed where electrical isolation of a portion of a pipeline is necessary to facilitate the application of corrosion control.

(c) Except for unprotected copper inserted in ferrous pipe, each pipeline must be electrically isolated from metallic casings that are a part of the underground system. However, if isolation is not achieved because it is impractical, other measures must be taken to minimize corrosion of the pipeline inside the casing.

(d) Inspection and electrical tests must be made to assure that electrical isolation is adequate.

(e) An insulating device may not be installed in an area where a combustible atmosphere is anticipated unless precautions are taken to prevent arcing.

(f) Where a pipeline is located in close proximity to electrical transmission tower footings, ground cables or counter-poise, or in other areas where fault currents or unusual risk of lightning may be anticipated, it must be provided with protection against damage due to fault currents or lightning, and protective measures must also be taken at insulating devices.

192.469 External corrosion control: test stations.

Except where impractical on offshore and wet marsh area pipelines, each pipeline under cathodic protection required by this subpart must have sufficient test stations or other contact points for electrical measurement to determine the adequacy of cathodic protection.

192.471 External corrosion control: test leads.

(a) Each test lead wire must be connected to the pipeline so as to remain mechanically secure and electrically conductive.

(b) Each test lead wire must be attached to the pipeline so as to minimize stress concentration on the pipe.

(c) Each bared test lead wire and bared metallic area at point of connection to the pipeline must be coated with an electrical insulating material compatible with the pipe coating and the insulation on the wire.

192.473 External corrosion control: interference currents.

(a) After July 31, 1973, each operator whose pipeline system is subjected to stray currents shall have in effect a continuing program to minimize the detrimental effects of such currents.

(b) Each impressed current type cathodic protection system or galvanic anode system must be designed and installed so as to minimize any adverse effects on existing adjacent underground metallic structures.

192.475 Internal corrosion control: general.

(a) After July 31, 1972, corrosive gas may not be transported by pipeline, unless the corrosive effect of the gas on the pipeline has been investigated and steps have been taken to minimize internal corrosion.

(b) Whenever any pipe is removed from a pipeline for any reason, the internal surface must be inspected for evidence of corrosion. If internal corrosion is found-

(1) The adjacent pipe must be investigated to determine the extent of internal corrosion;

(2) Replacement must be made to the extent required by the applicable paragraphs of 192.485, 192.487, or 192.489; and

(3) Steps must be taken to minimize the internal corrosion.

(c) Gas containing more than 0.1 grain of hydrogen sulfide per 100 standard cubic feet may not be stored in pipe-type or bottle-type holders.

192.477 Internal corrosion control: monitoring.

If corrosive gas is being transported, coupons or other suitable means must be used to determine the effectiveness of the steps taken to minimize internal corrosion. After July 31, 1972, each coupon or other means of monitoring internal corrosion must be checked at intervals not exceeding 6 months.

192.479 Atmospheric corrosion control: general.

(a) Pipelines installed after July 31, 1971. Each above-ground pipelines or portion of a pipeline installed after July 31, 1971 that is exposed to the atmosphere must be cleaned and either coated or jacketed with a material suit-

able for the prevention of atmospheric corrosion. An operator need not comply with this paragraph, if the operator can demonstrate by test, investigation, or experience in the area of application, that a corrosive atmosphere does not exist.

(b) Pipelines installed before August 1, 1971. Not later than August 1, 1974, each operator having an above-ground pipeline or portion of a pipeline installed before August 1, 1971 that is exposed to the atmosphere, shall-

(1) Determine the areas of atmospheric corrosion on the pipeline;

(2) If atmospheric corrosion is found, take remedial measures to the extent required by the applicable paragraphs of 192.485, 192.487, or 192.489; and

(3) Clean and either coat or jacket the areas of atmospheric corrosion on the pipeline with a material suitable for the prevention of atmospheric corrosion.

192.481 Atmospheric corrosion control: monitoring.

After meeting the requirements of paragraphs (a) and (b) of 192.479, each operator shall, at intervals not exceeding 3 years, reevaluate its above-ground pipelines or portions of pipelines that are exposed to the atmosphere and take remedial action wherever necessary to maintain protection against atmospheric corrosion.

192.483 Remedial measures: general.

(a) Each segment of metallic pipe that replaces pipe removed from a buried or submerged pipeline because of external corrosion must have a properly prepared surface and must be provided with an external protective coating that meets the requirements of 192.461.

(b) Each segment of metallic pipe that replaces pipe removed from a buried or submerged pipeline because of external corrosion must be cathodically protected in accordance with this subpart.

(c) Except for cast iron or ductile iron pipe, each segment of buried or submerged pipe that is required to be repaired because of external corrosion must be cathodically protected in accordance with this subpart.

192.485 Remedial measures: transmission lines.

(a) General corrosion. Each segment of transmission line pipe with general corrosion and with a remaining wall thickness less than that required for the maximum allowable operating pressure of the pipeline, must be replaced or the operating pressure reduced commensurate with the actual remaining wall thickness. However, if the area of

general corrosion is small, the corroded pipe may be repaired. Corrosion pitting so closely grouped as to affect the overall strength of the pipe is considered general corrosion for the purpose of this paragraph.

(b) Localized corrosion pitting. Each segment of transmission line pipe with localized corrosion pitting to a degree where leakage might result must be replaced or repaired, or the operating pressure must be reduced commensurate with the strength of the pipe, based on the actual remaining wall thickness in the pits.

192.487 Remedial measures: distribution lines other than cast iron or ductile iron lines.

(a) General corrosion. Except for cast iron or ductile iron pipe, each segment of generally corroded distribution line pipe with a remaining wall thickness less than that required for the maximum allowable operating pressure of the pipeline, or a remaining wall thickness less than 30 percent of the nominal wall thickness, must be replaced. However, if the area of general corrosion is small, the corroded pipe may be repaired. Corrosion pitting so closely grouped as to affect the overall strength of the pipe is considered general corrosion for the purpose of this paragraph.

(b) Localized corrosion pitting. Except for cast iron or ductile iron pipe, each segment of distribution line pipe with localized corrosion pitting to a degree where leakage might result must be replaced or repaired.

192.489 Remedial measures: cast iron and ductile iron pipelines.

(a) General graphitization. Each segment of cast iron or ductile iron pipe on which general graphitization is found to a degree where a fracture or any leakage might result, must be replaced.

(b) Localized graphitization. Each segment of cast iron or ductile iron pipe on which localized graphitization is found to a degree where any leakage might result, must be replaced or repaired, or sealed by internal sealing methods adequate to prevent or arrest any leakage.

192.491 Corrosion control records.

(a) After July 31, 1972, each operator shall maintain records or maps to show the location of cathodically protected piping, cathodic protection facilities, other than unrecorded galvanic anodes installed before August 1, 1971, and neighboring structures bonded to the cathodic protection system.

(b) Each of the following records must be retained for as long as the pipeline remains in service:

(1) Each record or map required by paragraph (a) of this section.

(2) Records of each test, survey, or inspection required by this subpart, in sufficient detail to demonstrate the adequacy of corrosion control measures or that a corrosive condition does not exist.

Appendix D-Criteria for Cathodic Protection and Determination of Measurements

I. Criteria for cathodic protection-A. Steel, cast iron, and ductile iron structures.

(1) A negative (cathodic) voltage of at least 0.85 volt, with reference to a saturated copper-copper sulfate half cell. Determination of this voltage must be made with the protective current applied, and in accordance with sections II and IV of this appendix.

(2) A negative (cathodic) voltage shift of at least 300 millivolts. Determination of this voltage shift must be made with the protective current applied, and in accordance with sections II and IV of this appendix. This criterion of voltage shift applies to structures not in contact with metals of different anodic potentials.

(3) A minimum negative (cathodic) polarization voltage shift of 100 millivolts. This polarization voltage shift must be determined in accordance with sections III and IV of this appendix.

(4) A voltage at least as negative (cathodic) as that originally established at the beginning of the Tafel segment of the E-log-I curve. This voltage must be measured in accordance with section IV of this appendix.

(5) A net protective current from the electrolyte into the structure surface as measured by an earth current technique applied at predetermined current discharge (anodic) points of the structure.

B. Aluminum structures. (1) Except as provided in subparagraphs (3) and (4) of this paragraph, a minimum negative (cathodic) voltage shift of 150 millivolts, produced by the application of protective current. The voltage shift must be determined in accordance with sections II and IV of this appendix.

(2) Except as provided in subparagraphs (3) and (4) of this paragraph, a minimum negative (cathodic) polarization voltage shift of 100 millivolts. This polarization voltage shift must be determined in accordance with sections III and IV of this appendix.

(3) Notwithstanding the alternative minimum criteria in subparagraphs (1) and (2) of this paragraph, aluminum, if cathodically protected at voltages in excess of 1.20 volts as measured with reference to a copper-copper sulfate half

cell, in accordance with section IV of this appendix, and compensated for the voltage (IR) drops other than those across the structure-electrolyte boundary, may suffer corrosion resulting from the build-up of alkali on the metal surface. A voltage in excess of 1.20 volts may not be used unless previous test results indicate no appreciable corrosion will occur in the particular environment.

(4) Since aluminum may suffer from corrosion under high pH conditions, and since application of cathodic protection tends to increase the pH at the metal surface, careful investigation or testing must be made before applying cathodic protection to stop pitting attack on aluminum structures in environments with a natural pH in excess of 8.

C. Copper structures. A minimum negative (cathodic) polarization voltage shift of 100 millivolts. This polarization voltage shift must be determined in accordance with sections III and IV of this appendix.

D. Metals of different anodic potentials. A negative (cathodic) voltage, measured in accordance with section IV of this appendix, equal to that required for the most anodic metal in the system must be maintained. If amphoteric structures are involved that could be damaged by high alkalinity covered by subparagraphs (3) and (4) of paragraph B of this section, they must be electrically isolated with insulating flanges, or the equivalent.

II. Interpretation of voltage measurement. Voltage (IR) drops other than those across the structure-electrolyte boundary must be considered for valid interpretation of the voltage measurement in paragraph A(1) and (2) and paragraph B(1) of section 1 of this appendix.

III. Determination of polarization voltage shift. The polarization voltage shift must be determined by interrupting the protective current and measuring the polarization decay. When the current is initially interrupted, an immediate voltage shift occurs. The voltage reading after the immediate shift must be used as the base reading from which to measure polarization decay in paragraphs A(3), B(2), and C of section 1 of this appendix.

IV. Reference half cells. A. Except as provided in paragraphs B and C of this section, negative (cathodic) voltage must be measured between the structure surface and a saturated copper-copper sulfate half cell contacting the electrolyte.

B. Other standard reference half cells may be substituted for the saturated copper-copper sulfate half cell. Two commonly used reference half cells are listed below along with their voltage equivalent to -0.85 volt as referred to a saturated copper-copper sulfate half cell:

- (1) Saturated KCl calomel half cell: -0.78 volt.
- (2) Silver-silver chloride half cell used in sea water: -0.80 volt.

C. In addition to the standard reference half cells, an alternate metallic material or structure may be used in place of the saturated copper-copper sulfate half cell if its potential stability is assured and if its voltage equivalent referred to a saturated copper-copper sulfate half cell is established.

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TRANSPORTATION OF LIQUIDS BY PIPELINE*

SUBPART A -- GENERAL

AFFECTED FACILITIES

195.1 Scope.

(a) Except as provided in paragraph (b) of this section, this part prescribes rules governing the transportation by pipeline in interstate and foreign commerce of hazardous materials that are subject to Parts 172 and 173 of this chapter, petroleum, and petroleum products.

(b) This part does not apply to-

(1) Transportation of water or any commodity that is transported in a gaseous state;

(2) Transportation through a pipeline by gravity;

(3) Transportation through pipelines that operate at a stress level of 20 percent or less of the specified minimum yield strength of the line pipe in the system; and

(4) Except for Subpart B of this part, transportation of petroleum in rural areas between a production facility and the point where the petroleum is received by a carrier.

SUBPART D -- CONSTRUCTION

REQUIRED PROTECTIVE MEASURES

195.236 External corrosion protection.

Each component in the pipeline system must be provided with protection against external corrosion.

195.238 External coating.

(a) No pipeline system component may be buried unless that component has an external protective coating that-

(1) Is designed to mitigate corrosion on the buried component;

(2) Has sufficient adhesion to the metal surface to prevent underfilm migration of moisture;

(3) Is sufficiently ductile to resist cracking;

(4) Has enough strength to resist damage due to handling

and soil stress; and

(5) Supports any supplemental cathodic protection. In addition, if an insulating-type coating is used it must have low moisture absorption and provide high electrical resistance.

(b) All pipe coating must be inspected just prior to lowering the pipe into the ditch and any damage discovered must be repaired.

195.242 Cathodic protection system.

(a) A cathodic protection system must be installed for all buried facilities to mitigate corrosion deterioration that might result in structural failure. A test procedure must be developed to determine whether adequate cathodic protection has been achieved.

(b) A cathodic protection system must be installed not later than 1 year after completing the construction.

195.244 Test leads.

(a) Except for offshore pipelines, electrical test leads used for corrosion control or electrolysis testing must be installed at intervals frequent enough to obtain electrical measurements indicating the adequacy of the cathodic protection.

(b) Test leads must be installed as follows:

(1) Enough looping or slack must be provided to prevent test leads from being unduly stressed or broken during back filling.

(2) Each lead must be attached to the pipe so as to prevent stress concentration on the pipe.

(3) Each lead installed in a conduit must be suitably insulated from the conduit.

SUBPART F -- OPERATION AND MAINTENANCE

CATHODIC PROTECTION REQUIREMENTS

195.414 Cathodic protection.

(a) After March 31, 1973, no carrier may operate a pipeline that has an external surface coating material, unless that pipeline is cathodically protected. This paragraph does not apply to tank farms and buried pumping station piping.

(b) Each carrier shall electrically inspect each bare pipeline before April 1, 1975, to determine any areas in which active corrosion is taking place. The carrier may not increase its established maximum operating pressure on a section of bare pipeline until the section has been so electrically inspected. In any areas where active corrosion is found, the carrier shall provide cathodic protection.

Section 195.416 (f) and (g) applies to all corroded pipe that is found.

(c) Each carrier shall electrically inspect all tank farms and buried pumping station piping before April 1, 1973, as to the need for cathodic protection, and cathodic protection shall be provided where necessary.

EXTERNAL CORROSION CONTROL

TESTING AND INSPECTION

195.416 External corrosion control.

(a) Each carrier shall, at intervals not exceeding 12 months, conduct tests on each underground facility in its pipeline systems that is under cathodic protection to determine whether the protection is adequate.

(b) Each carrier shall maintain the test leads required for cathodic protection in such a condition that electrical measurements can be obtained to ensure adequate protection.

(c) Each carrier shall, at intervals not exceeding 2 months, inspect each of its cathodic protection rectifiers.

(d) Each carrier shall, at intervals not exceeding 5 years, electrically inspect the bare pipe in its pipeline system that is not cathodically protected and must study leak records for that pipe to determine if additional protection is needed.

(e) Whenever any buried pipe is exposed for any reason, the carrier shall examine the pipe for evidence of external corrosion. If the carrier finds that there is active corrosion, that the surface of the pipe is generally pitted, or that corrosion has caused a leak, it shall investigate further to determine the extent of the corrosion.

(f) Any pipe that is found to be generally corroded so that the remaining wall thickness is less than the minimum thickness required by the pipe specification tolerances must either be replaced with coated pipe that needs the requirements of this part or, if the area is small, must be repaired. However, the carrier need not replace generally corroded pipe if the operating pressure is reduced to be commensurate with the limits on operating pressure specified in this subpart, based on the actual remaining wall thickness.

(g) If isolated corrosion pitting is found, the carrier shall repair or replace the pipe unless-

(1) The diameter of the corrosion pits, as measured at the surface of the pipe, is less than the nominal wall thickness of the pipe; and

(2) The remaining wall thickness at the bottom of the pits is at least 70 percent of the nominal wall thickness.

(h) Each carrier shall clean, coat with material suitable for the prevention of atmospheric corrosion, and, maintain

this protection for, each component in its pipeline system that is exposed to the atmosphere.

INTERNAL CORROSION CONTROL

195.418 Internal corrosion control.

(a) No carrier may transport any commodity that would corrode the pipe or other components of its pipeline system, unless it has investigated the corrosive effect of the commodity on the system and has taken adequate steps to mitigate corrosion.

(b) If corrosion inhibitors are used to mitigate internal corrosion the carrier shall use inhibitors in sufficient quantity to protect the entire part of the system that the inhibitors are designed to protect and shall also use coupons or other monitoring equipment to determine their effectiveness.

(c) The carrier shall, at intervals not exceeding 6 months, examine coupons or other types of monitoring equipment to determine the effectiveness of the inhibitors or the extent of any corrosion.

(d) Whenever any pipe is removed from the pipeline for any reason, the carrier must inspect the internal surface for evidence of corrosion. If the pipe is generally corroded such that the remaining wall thickness is less than the minimum thickness required by the pipe specification tolerances, the carrier shall investigate adjacent pipe to determine the extent of the corrosion. The corroded pipe must be replaced with pipe that meets the requirements of this part.

(*) Excerpt from Federal Register, October 4, 1969, Title 49 - Transportation, Part 195 - Transportation of Liquids by Pipeline.

APPENDIX C.

ELECTROMOTIVE FORCE SERIES

Electrode Reaction	Standard Electrode Potential E^0 (volts), 25°C .
Potassium = $\text{K}^+ + \text{e}^-$	-2.922
Calcium = $\text{Ca}^{++} + 2\text{e}^-$	-2.87
Sodium = $\text{Na}^+ + \text{e}^-$	-2.712
Magnesium = $\text{Mg}^{++} + 2\text{e}^-$	-2.34
Beryllium = $\text{Be}^{++} + 2\text{e}^-$	-1.70
Aluminum = $\text{Al}^{+++} + 3\text{e}^-$	-1.67
Manganese = $\text{Mn}^{++} + 2\text{e}^-$	-1.05
Zinc = $\text{Zn}^{++} + 2\text{e}^-$	-0.762
Chromium = $\text{Cr}^{+++} + 3\text{e}^-$	-0.71
Gallium = $\text{Ga}^{+++} + 3\text{e}^-$	-0.52
Iron = $\text{Fe}^{++} + 2\text{e}^-$	-0.440
Cadmium = $\text{Cd}^{++} + 2\text{e}^-$	-0.402
Indium = $\text{In}^{+++} + 3\text{e}^-$	-0.340
Thallium = $\text{Tl}^+ + \text{e}^-$	-0.336
Cobalt = $\text{Co}^{++} + 2\text{e}^-$	-0.277
Nickel = $\text{Ni}^{++} + 2\text{e}^-$	-0.250
Tin = $\text{Sn}^{++} + 2\text{e}^-$	-0.136
Lead = $\text{Pb}^{++} + 2\text{e}^-$	-0.126
Hydrogen = $2\text{H}^+ + 2\text{e}^-$	0.000
Copper = $\text{Cu}^{++} + 2\text{e}^-$	0.345
Copper = $\text{Cu}^+ + \text{e}^-$	0.522
Mercury = $\text{Hg}_2^{++} + 2\text{e}^-$	0.799
Silver = $\text{Ag}^+ + \text{e}^-$	0.800
Palladium = $\text{Pd}^{++} + 2\text{e}^-$	0.83
Mercury = $\text{Hg}^{++} + 2\text{e}^-$	0.854
Platinum = $\text{Pt}^{++} + 2\text{e}^-$	1.2
Gold = $\text{Au}^{+++} + 3\text{e}^-$	1.42
Gold = $\text{Au}^+ + \text{e}^-$	1.68

TABLE D-1 (Continued)

GALVANIC SERIES WITH RESPECT
TO SATURATED CALOMEL ELECTRODE¹

<u>Metal</u>	<u>Negative Potential to Saturated Calomel Electrode, volts¹</u>
Nickel	0.20
Stainless steel type 316, 18% Cr, 12% Ni, 3% Mo (active)	0.18
Inconel	0.17
Stainless steel type 410, 13% Cr (passive)	0.15
Titanium (commercial)	0.15
Silver	0.13
Titanium (high purity from iodide)	0.10
Stainless steel type 304, 18% Cr, 8% Ni (passive)	0.08
Hastelloy C	0.08
Monel	0.08
Stainless steel type 316, 18% Cr 12% Ni, 3% Mo (passive)	0.05

¹ Based on potential measurements in sea water; velocity of flow, 13 ft. per sec.; temperature 25°C. (77°F.).

APPENDIX D.

TABLE D-1

GALVANIC SERIES WITH RESPECT
TO SATURATED CALOMEL ELECTRODE¹

Metal	Negative Potential to Saturated Calomel Electrode, volts ¹
Zinc	1.03
Aluminum (Alclad 3S)	0.94
Aluminum (3S-H)	0.79
Aluminum (61S-T)	0.76
Aluminum (52S-H)	0.74
Cast iron	0.61
Carbon steel	0.61
Stainless steel type 430	
17% Cr (active)	0.57
Ni-resist cast iron, 20% Ni	0.54
Stainless steel type 304	
18% Cr, 8% Ni (active)	0.53
Stainless steel type 410,	
13% Cr (active)	0.52
Ni-resist cast iron, 30% Ni	0.49
Ni-resist cast iron, 30% Ni + Cu	0.46
Naval rolled brass	0.40
Yellow brass	0.36
Copper	0.36
Red brass	0.33
Composition G bronze	0.31
Admiralty brass	0.29
90-10 Cupro nickel, 0.8% iron	0.28
70-30 Cupro nickel, 0.06% iron	0.27
70-30 Cupro nickel, 0.47% iron	0.25
Stainless steel type 430,	
17% Cr (passive)	0.22

¹ Based on potential measurements in sea water; velocity of flow, 13 ft. per sec.; temperature 25°C. (77°F).

TABLE D-2
GALVANIC SERIES WITH RESPECT TO
SATURATED COPPER-COPPER SULFATE ELECTRODE¹

Metal	Negative Potential to Saturated Copper-Copper Sulfate electrode
Magnesium (Galvomag alloy) ^a	1.75
Magnesium (H-1 alloy) ^a	1.55
Zinc	1.10
Aluminum (Alclad 3S)	1.01
Cast iron	0.68
Carbon steel	0.68
Stainless steel type 430, 17% Cr ^b	0.64
Ni-resist cast iron, 20% Ni	0.61
Stainless steel type 304, 18% Cr, 8% Ni ^b	0.60
Stainless steel type 410, 13% Cr ^b	0.59
Ni-resist cast iron, 30% Ni	0.56
Ni-resist cast iron, 20% Ni + Cu	0.53
Naval rolled brass	0.47
Yellow brass	0.43
Copper	0.43
Red brass	0.40
Bronze, composition G	0.38
Admiralty brass	0.36
90:10 Cu-Ni + 0.8% Fe	0.35
70:30 Cu-Ni + 0.06% Fe	0.34
70:30 Cu-Ni + 0.47% Fe	0.32
Stainless steel type 430, 17% Cr ^b	0.29
Nickel	0.27
Stainless steel type 316, 18% Cr, 12% Ni, 3% Mo ^b	0.25
Inconel	0.24
Stainless steel type 410, 13% Cr ^b	0.22
Titanium (commercial)	0.22
Silver	0.20
Titanium (high purity from iodide)	0.17
Stainless steel type 304, 18% Cr, 8% Ni ^b	0.15
Hastelloy C	0.15
Monel	0.15
Stainless steel type 316, 18% Cr, 12% Ni, 3% Mo ^b	0.12

¹ Based on potential measurements in sea water; velocity of flow, 13 ft. per sec.; temperature 25°C. (77°F).

^a Based on data by The Dow Chemical Company.

^b The stainless steels as a class exhibited erratic potentials depending on the incidence of pitting and corrosion in the crevices formed around the specimen supports. The values listed represent the extremes observed and, due to their erratic nature, should not be considered as establishing an invariable potential reaction among the alloys which are covered.

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